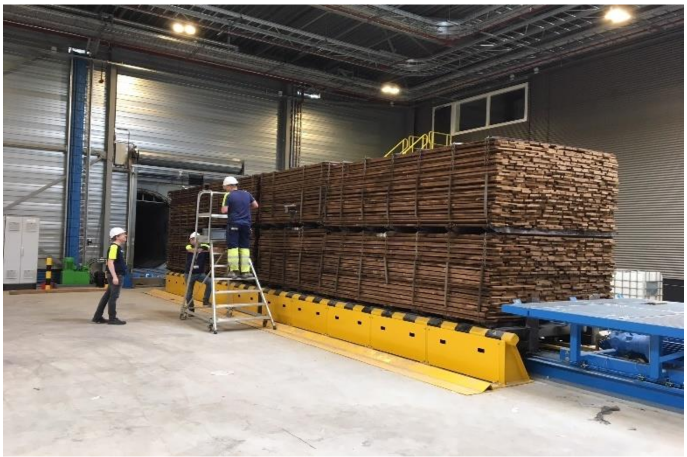
9th European Conference on Wood Modification
ECWM9

September 17 and 18, 2018, Arnhem, The Netherlands

PROCEEDINGS



SHR

ECWM9

The 9th European Conference on **Wood** Modification

The Netherlands • Arnhem • September 17-18, 2018

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9th European Conference on Wood Modification

Burgers' Zoo
Arnhem, The Netherlands
17-18 September 2018

In association with:
COST FP1407 ModWoodLife

Edited by:
Jos Creemers, Thomas Houben, Bôke Tjeerdsma, Holger Militz, Brigitte Junge and Jos Gootjes

Secretariat:
SHR B.V.
Nieuwe Kanaal 9b
6709 PA Wageningen
www.ecwm9.shr.nl

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Preface

SHR was one of the first research institutes in Europe, who already in the 1990´s did substantial research work to develop wood modification processes. It appeared, that this research area was very complex, and that for a successful application of potential processes different expertise’s was needed. A good network between research partners and industry was needed and the “European Network on Wood Modification” was created. 15 years ago, in 2003, the first European Conference on Wood Modification “ECWM” was held to present the outcomes of this EU financed network. Since than, ECWM´s were held each 2-3 years at different places around Europe, and now we can celebrate the 9th ECWM in the Netherlands, organized by SHR where it all began.

As already before, ECWM 9 is linked up to the European COST organisation. Thanks to the COST Action FP 1407 ModWoodLife to join and strengthen our network!

The participation of researchers of all around the world make it obvious that the name “European conference” is much too small…so: a warm welcome to researchers from industry and academia from Europe and abroad! This success has led, once again, to a large number of abstracts submitted to the organizers. In general, these abstracts were of a high quality and the members of the Scientific Committee had a hard time to select 44 full presentations and 50 poster presentations out of the many applications. We hope we have found the right balance between scientific and applied presentations to reach the key goal of ECWM: to attract researchers from academia and industry to join their expertises in this very exciting research area “wood modification”.

The local conference organizers from SHR have done a great job this past year to make us feel welcome in The Netherlands and to let the conference be a success. Thank you very much to Bôke and team!

Holger Militz

Prof. Dr. Holger Militz
Chairman of Scientific Committee
Georg-August-University Göttingen, Germany

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Wood modification in practice

The European Conference on Wood Modification takes place on the 17th and 18th of September 2018 in Arnhem, The Netherlands and is organised by SHR. At this conference researchers and people from industry from all over the world will come together to share their knowledge and experiences with the latest developments on wood modification methods, applications and products. The conference was given the subtitle “Wood modification comes home”, which refers to the role The Netherlands and SHR have played – and still play – in the development and industrial application of modified wood.

Techniques and methods designed for improving wood properties are almost as old as mankind itself. However the scientific and industrial rise of wood modification became significant under the influence of a number of social and economic developments in the eighties and nineties of the previous century. A strong need was felt to find alternatives for the use of tropical hardwoods and preservative treated wood, which were both under pressure for a variety of reasons. The discussions regarding a clean environment, sustainable forest management, wood use and the increasing wood demands from emerging markets in Asia also had a big impact. Wood modification was recognized to have the ability to offer a more, better and sustainable way of making use of wood as a durable material in a broad range of applications. Besides that, it was found to be a supreme method for upgrading the properties of lesser used timber species and to provide technical solutions to overcome some of the natural deficiencies of wood as water uptake, decay and dimensional changes.

Over the last decades an enormous amount of scientific work has been performed and published. We have seen many innovative modification ideas, methods and techniques passing by during the previous eight ECWM’s. To make a real impact, ideas need to be developed further and put into practice. We are proud that in The Netherlands we have created a setting with a high level of knowledge, innovative thinking combined with entrepreneurship, which lead to a variety of flourishing companies involved in industrial production of modified wood. Not only producing companies, but also the wood processing industry has adopted modified wood as a highly appreciated durable material. We can declare that modified wood has become a lasting factor in the wood processing industry.

For these reasons SHR and we as the organising team, are excited to welcome you all here in The Netherlands for the 9th European Conference on Wood Modification. We hope you will enjoy your stay here in Arnhem and become inspired by all attendees, presenters and new insights this conference has to offer.

Welcome!

The organising team

COST 1407 - Foreword

It is our pleasure that COST Action FP1407 “Understanding wood modification through an integrated scientific and environmental impact approach” (ModWoodLife) in part of 9th European Conference of Wood Modification. The conference brings together researchers from across Europe and beyond that jointly are addressing the mounting pressure on renewable resources (as a material source, for recreational, ecological, and other uses). By maximising the efficiency of materials derived from them, the wood modification community plays an important role. The efficiency can only be achieved if new methods to improve the functionality, durability, properties, and environmental impacts will be developed. Wood modification addresses these requirements directly, allowing wood to be used in more applications, including increased use of under-utilised species. Wood modification also addresses undesirable characteristics of wood such as fungal resistance, UV-stability, and moisture sensitivity. The COST Action FP1407 has been successful in addressing these needs in the past 3 years. We are in the last year of the Action and therefore it is even more important for us to be at ECWM9. Only sustainable collaboration and joint efforts will deliver the impacts. That objective of the Action FP1407, to characterise the relationship between wood modification processing, product properties, and the associated environmental impacts in order to maximise sustainability and minimize environmental impacts, has great value for the forest sector, for researchers, and society at large.

Wishing you a successful and memorable conference full of fruitful discussions.

Andreja Kutnar
Chair, COST FP1407

Denis Jones
Vice-Chair, COST FP1407

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SESSION ONE

Wood Modification world-wide - Keynote presentations

Modified wood in circular economy – a critical review

Henrik Heräjärvi[1,3], Janni Kunttu[2], Elias Hurmekoski[2] & Teppo Hujala[1,3]

[1]University of Eastern Finland, School of Forest Sciences, Yliopistokatu 7, FIN-80101 Joensuu, Finland [email: henrik.herjarvi@uef.fi]
[2]European Forest Instititute, Yliopistokatu 6, FIN-80101 Joensuu, Finland [email: janni.kunttu@efi.int]

[3]Natural Resources Institute Finland, Yliopistokatu 6, FIN-80101 Joensuu, Finland [email: teppo.hujala@luke.fi]

Keywords: cascading, circular economy, modified wood, recycling, resource efficiency.

ABSTRACT

The European Union aims at development towards a circular economy. In practice, this stands for increasing the resource efficiency by waste minimization in production processes, cascade uses of materials, elimination of landfill wastes, and maximizing the value of the raw materials. The same general policy concerns materials independently on their origin, *i.e.*, whether they are renewable or non-renewable. The idea is good and worth making considerable economic and ecological efforts, but also sets transformation challenges to the societies and industries. These challenges have, furthermore, country-specific differences depending on the production structure, environmental circumstances, local policies and regulations, as well as economic resources. The key indicator for resource efficiency is €/kg, which allows pursuing increased efficiency by minimizing material input (and waste) and/or by maximizing value. In case of modified wood, these two approaches may be of positive character, even an opportunity. Modified wood plays an almost insignificant role in the circular economy discourse, but circular economy may play a major role in wood modification businesses. The objective of this paper is to review the renewed waste management legislation in the European Union and analyze the possible future effects of circular economy development in Europe on wood modification both from viewpoints of the existing products and technologies and the emerging ones. Finland is given as an example of a country with strong wood modification industries and great expected impacts caused by the circular economy development.

NEW WASTE LEGISLATION IN THE EUROPEAN UNION

Re-using means that the material or product is used in the same end use for a second time. Recycling means that the material or product is used in a different end use after its primary use. Circulation, in turn, refers to the processes of re-using and recycling in circular economy system. In this article, we use the term "waste" for all materials after their primary use. Thus, "*waste*" includes both landfill waste and recovered materials collected for re-use, recycling, or energy production.

Many European Union member states have gradually improved their waste management practices in accordance with the EU waste hierarchy principle (Figure 1) during the last two decades. On the average, 64 per cent of municipal waste ended up in landfills in the European Union in 1995. Five years later the percentage was 55, and the share of recycled waste was 25%. According to the latest available statistics, the percentages of household waste ending up in landfills and recycling in the EU in 2016 were 24 and 46, respectively. There are, however, great country-to-country differences. The share of landfilled household waste still exceeds 50% in ten EU countries.

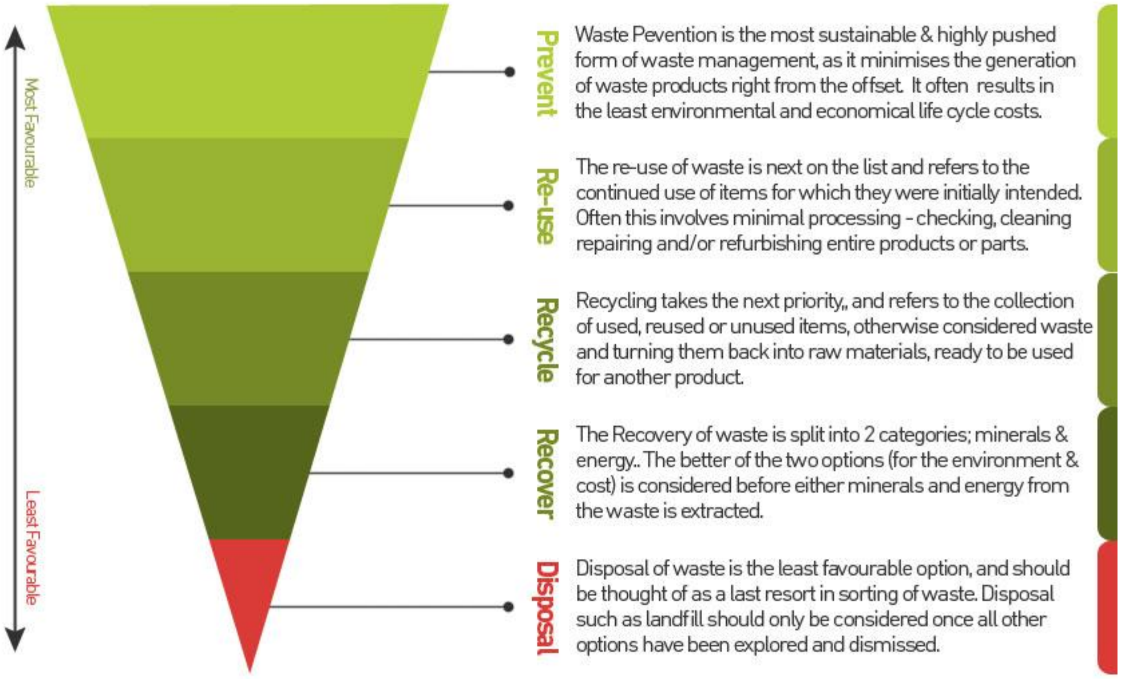

Figure 1: The European Union Waste Hierarchy principle. Source: http://www.direct365.co.uk/blog/wp-content/uploads/2014/05/Waste-Hierarchy.jpg

The new ambitious waste directives (http://europa.eu/rapid/press-release_IP-18-3846_fi.htm) of the European Union, accepted on 22nd of May 2018, aim at preventing waste generation. When it is not possible, such as in case of packaging and municipal waste, recycling is supported. The original proposition of the European Commission from year 2015 was a part of the Circular Economy Package (http://europa.eu/rapid/press-release_IP-15-6203_en.htm), where one of the key aims is gradual decrease of the volume of landfill waste. Now the new legislation commits the member states to waste generation prevention, re-use of materials, and recycling of them instead of incineration and landfilling. Landfilling of wastes is not seen rational in a circular economy due to the resulting pollution of water, soil, and atmosphere. The new obligations are supposed to stimulate the transition of the EU to put the circular economy into practice. The Circular Economy Package indicates that the EU seriously aims at economic transformation via new business opportunities and increased competitiveness that result from fundamental changes in the concept of product lifecycle. Development is expected both in production and consumption practices, which means systemic transformation challenge.

According to the European Commission, the new waste legislation is the most forward-looking one in the World, and gives the EU a reason to act as a model to other countries. The aim is to recycle 55, 60, and 65 per cent of the municipal waste in years 2025, 2030, and 2035, respectively. Only maximum ten per cent of the municipal waste can be landfilled in 2035. With regard to packaging materials, improvement in recycling rate of solid wood waste is still rather modest in comparison to many other materials (Table 1).

Table 1: Recycling objectives of different packaging materials in the EU in 2025 and 2030 (http://europa.eu/rapid/press-release_IP-18-3846_en.htm).

Year	**2025**	**2030**
	Recycled [%]	
Plastic	50	55
Wooden	25	30
Iron/Steel	70	80
Aluminum	50	60
Glass	70	75
Paper and paperboards	75	85
All packages	*65*	*70*

Already the previous waste legislation obliged the EU member states to organize recycling of paper, paperboard, glass, metal, and plastic wastes. The new obligations aim at further improvement of the quality and usability of wastes, transforming them into materials. Separate recycling systems will be required for dangerous household wastes in 2022, organic wastes in 2023, and textile wastes in 2025. In addition, there will be a ban on landfilling of separately collected waste. Material re-use and industrial symbiosis, *i.e.*, turning one industry's by-product into another industry's raw material, and forming new business collaborations around this activity, have very high rank among the promoted actions of the waste legislation. The new legislation relies mainly on economic guidance and incentives that support the countries to follow the waste hierarchy. In addition to the national investments, there are 650 million € Horizon 2020 funding and 5.5 billion € from EU structural funds allocated for waste management development in the circular economy. Presumably there will be funding instruments designated into these topics also within the next framework program.

The producer responsibility principle will be extended from its current status in order to improve its effectiveness and administration. In practice, manufacturers are bound to manage product's re-use or recycling after its primary life cycle, *i.e.*, closing the loop. Producer responsibility systems will be required for instance from producers of packaging materials in year 2024. Organizing re-use or recycling of the packaging materials is expensive, particularly in sparsely populated areas, and it is rather evident that consumers will pay these investments, finally. The aim of the European waste hierarchy principle and waste legislation being high-minded, *i.e.*, extracting the maximum value and use from all raw materials, products, and wastes, fostering energy savings, and reducing CO_2 emissions, there are still many problems involved. Implementation of the waste legislation requires that each country set clear targets for waste reduction. A credible long-term waste management and recycling strategy is necessary in order to achieve the targets. In terms of product manufacturing, this means that not only energy efficiency and durability but also reparability and recyclability of products have to be considered more thoroughly than before. These increasing requirements may cause resistance among industries who have not circulation in the core of their existing business model and who, thus, consider their market position threatened. However, the policy signs towards closed loops are so strong that anticipatory and agile firms likely succeed in the transformation. Finally, waste legislation sets a need for new simpler and univocal definitions as well as harmonized calculation methods for recycling rates throughout the EU.

From the viewpoint of wood product industries and especially wood modification business, there is one particularly interesting statement published along with the waste legislation information. It indicates that there will be economic incentives for manufacturers who provide markets with greener products and support recovery and recycling schemes. If operationalized in a meaningful manner, this is likely to cease resistance and facilitate wood product industries in transformation to circular economy.

The available range of commercial wood products has increased by some innovations during the 2000s. One category is wood-based composites and another is modified wood products. This article reviews the questions and challenges related to circular economy development from the viewpoint of modified wood products. We discuss facts related to waste management and recycling and draw conclusions related to modified wood products.

MODIFIED WOOD PRODUCTS IN CIRCULAR ECONOMY

Most of the wood waste from building construction and demolition sites ends up to energy production in northern Europe. In southern and central Europe, on the other hand, the majority of the recovered wood goes to particle and fibreboard production (*e.g.*, Heräjärvi *et al.* 2010ab). Modified wood products have become a 'new normal' in consumer markets during this millennium. A common feature to all modified wood products is that their lifetime is preferably longer than that of an unmodified product (*e.g.*, Hill 2006, Sandberg *et al.* 2017, Möttönen *et al.* 2018). From durability point of view, the maximum attainable lifetime is not realised in products intended to, *e.g.*, fashion dependent applications, such as interior decorations, or products that are completely replaced after a minor damage in a limited area, such as decking or cladding. The same is true in some demanding load-bearing structures that are exposed to weather, such as bridges and traffic barriers: highway traffic barriers have to be replaced even after a minor damage. This means that a considerable proportion of the replaced material is in a relatively good condition for either re-use in less demanding structures or recycling. If wood modification causes even minor restrictions to the possibilities to re-use or recycle it, modification ultimately impairs the material's life cycle performance relative to normal wood products that do not suffer from such restrictions. Hence, the actualised product lifetime, as well as its environmental performance, depend on the type of its use and success in streamlining the cascading principle in the production and consumption system.

Modified wood products already have, and will further effect on the recyclability of wood products and structures, thus also effecting on their environmental footprint in comparison to products made of other materials or non-modified wood. Heräjärvi *et al.* (2010b) paid attention to the fact that not much work was devoted to the possibilities and challenges in re-use and recycling of modified wood. This concern, presented in ECWM5 conference in Riga in 2010, is even more topical now because of the renewed waste legislation and circular economy strategy of the European Union. The idea of improved recyclability favours materials that have higher durability than the competing ones. The most valuable wastes are the most efficiently recycled. In addition to private companies, public actors (state, municipalities) have a very strong role in circular economy development in terms of tenders and sustainable product procurement.

The green building certification systems, such as LEED, also set requirements for the raw materials used in construction or renovation (see *e.g.*,: https://www.wbdg.org/resources/green-building-standards-and-certification-systems). One of the elements considered when applying for green building certificate is the proportion of recycled materials used in the buildings. If modified wood products do not have advanced-enough recycling or re-using systems, they lose their competitiveness in green building certificate systems.

Products' resistance against decay, mold, or insects, as well as its durability against moisture, UV radiation, and fluctuating temperatures are features in keeping with the end uses of modified wood products: all modification methods aim at improving one or several of these properties (Table 2). The improvement can be achieved with (*e.g.*, Belmadur®, Accoya) or without (*e.g.*, Thermowood®) added chemicals. Obviously, also secondary products made of recovered modified wood will perform differently than unmodified products, which sets interesting research and product development challenges. With some preconditions related to management and control of possible chemical treatments or coatings applied, modified wood products can be used in particleboard or fiberboard production after their primary life cycle. Once recycled into new products, modified wood can provide the panel industries with raw materials that have unconventional stability, durability, or emission properties, for instance.

Table 2: General property requirements of modified wood products by end use category. Explanations: +++ (very important or a precondition); ++ (important); + (necessary); – (usually unnecessary). Table adopted and updated from the original of Heräjärvi et al. (2010b).

End use group	**Property group**						
	Resistance against			Strength	Appearance	Dimensional stability	Treatability (paint, *etc.*)
	Weather / UV-light	Abrasion	Decay, mold or insects				
Cladding	+++	–	++	–	++	++	+++
Decking	+++	++	++	+	++	+	++
Garden furniture	++	+	++	++	++	+	+
Interior furniture	–	+	–	++	+++	+	+
Fixture or cabinet	–	–	+	+	++	++	+
Utility poles	+++	+	+++	+++	+	–	–
Other exterior uses1)	+	–	++	+	+	+	++
Marine structures	+	+	+++	+	+	+	+

1) *Such as fences, poles, posts, pergolas, etc.*

ThermoWood® with its almost 200,000 m^3 annual production (Fig. 2) is the most widespread modified wood product, so far. Therefore, it was chosen as an example of a product that not only contributes to the circular economy development but is also strongly affected by it.

Production of ThermoWood® also results in annual output of 3,000-6,000 tons of thermally modified residues (sawdust, shavings, cut-offs), which are partly used in composite manufacturing but mostly burned for energy production. TWPC (ThermoWood Plastic Composite) by Lunawood Ltd, for example, utilizes sawdust and shavings of thermally modified solid wood (www.lunawood.com/composite), which provides the TWPC composite with better dimensional stability than ordinary wood. Special products based on modified wood residues or recovered modified wood could be an interesting option in small-scale production. Since the conventional production of wood-based panels is typically in a scale of tens or hundreds of thousands of cubic meters, the output of modified wood residues is still far too small to feed a continuous wood-based panel production.

Strong political guidance and clear regulations presumably result in a situation where circular economy discourse has more visible role in media. This may contribute to the renewal of the business models, generate new firms that take advantage of the circular economy principles, and, in particular, change the consumer behaviour. We expect that pricing mechanisms guide the consumer behaviour more strongly towards circular economy in the future. We expect that the systemic transformation will actualise in a way that recyclable modified wood products have both positive image features and competitive pricing, which improves their market position and further facilitates the systemic transformation.

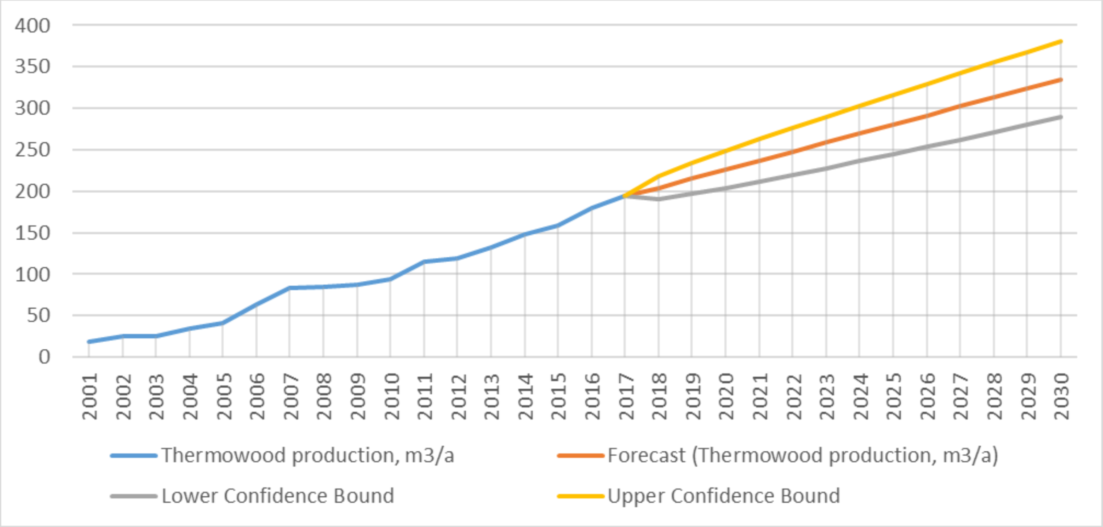

Figure 2: Production of thermally modified wood by the member companies of International Thermowood® Association between 2001 and 2017 (www.thermowood.fi), and linearly extrapolated production trend forecast up to 2030.

One of the core aims of circular economy is to maximize the circulation of products, components, and material flows by recycling, reuse, and sharing (Sitra 2016). The European Commission defines €/kg as a key indicator for circular economy. Optimizing the value of this indicator requires either reducing material input (and consequently waste) or increasing the value of materials (EC 2015). The scoring for modified wood depends on what it replaces. If it replaces plastic, for example in terraces, both the price and the material input may be higher, leading to no real advantage. Compared to unmodified wood, the densities do not typically differ, but the value can be multiplied for modified wood. However, such indicators may be of interest only on the level of countries or product specific functional units. For example, substituting concrete in construction can be highly beneficial, as it essentially reduces the total material input to a building without affecting too much the value of the building, *i.e.*, it avoids greater material use and waste due to different material densities. A lighter structural frame also allows reduced material input to the foundation.

Although modified wood still plays a minor role in the circular economy to date, the market share of products, such as wood composites, is likely to increase in the future (Kunttu *et al*. unpublished). This means that waste recycling may have a bigger role increasing the raw material availability in the wood modification industry. Market based solutions, such as Green building certificates, support the market share increment of modified wood products. Long-lifetime uses such as wooden building construction, is preferred over short-time uses. Short-time uses lose the advantages of long-lifetime modified wood products, and may lead to increased amount of waste wood. Recycling opportunities for modified wood products are necessary, in any case. Wood-base panel industries could use recycled modified wood as a raw material, but other solutions are required in countries, where panel industries is marginal or does not exist. Another question is, how to ensure the safety of recycled raw material and prevent dangerous glues or compounds ending up in in-house furniture and decorates. Currently, there are no binding waste wood classification systems in Europe, and traceability of materials becomes difficult. However, if the share of modified wood in recycling systems remains low, it helps testing and tracing the ingredients used in those products.

It is probable that a harmonised waste grading system will be developed in Europe soon to replace the existing various national systems. Harmonised waste classification would help in many ways. One critical advantage is collection of statistical information. This would enable effective regulative guidance and policy actions that promote circular economy development, and finally, generate business and markets around wastes.

CONCLUSIONS

In terms of wood-based waste management, most work is needed with construction and demolition wastes. Among other things, the green building certification systems call for recycled materials. We should gradually set the focus on savings, energy efficiency, and durable products with high recyclability and optimizing circulation in the production-consumption system. Modified wood products can and will be a crucial part of this development. Attention should be addressed also to development of recycled wood products that take the advantage of the chemical involved in the recovered raw materials. If the environmental risks caused by the chemicals in recovered wood are low enough, these materials can be used in civil engineering and earth structures, for instance as a lightening component of crushed concrete, rock, or stone materials. This could be beneficial not only in terms of material properties but also with regard to logistics costs. Environmental problems caused by excavation of virgin mineral materials would decrease to some extent, too.

Modified wood plays a minor role in the circular economy development. However, the circular economy development will apparently play an essential role in the wood modification businesses and their transformation along the anticipated systemic change. From the viewpoint of wood modification, there is one particularly interesting statement published along with the renewed EU waste legislation. It indicates that there will be economic incentives for manufacturers who provide markets with greener products and support material recovery and recycling schemes. It will be worth following to see, which instruments the European Commission and member states will finally implement. Circular economy development offers plenty of business opportunities and the EU policies support it. However, there are also hindrances and pitfalls that need to be foresighted and tackled. Here, collaboration between research, policy, and business is of vital importance.

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A Review of Wood Modification across Europe as Part of COST FP1407

Dennis Jones[1,2], Dick Sandberg[3] and Andreja Kutnar[4,5]

[1]DJ Timber Consultancy Ltd, 15 Heol Pen Y Coed, Neath, SA11 3SP United Kingdom [email: dr_dennisjones@hotmail.co.uk]
[2]Wood Science and Engineering, Luleå University of Technology, Forskargatan 1, S-93197 Skellefteå, Sweden [email: dennis.jones@ltu.se]
[3]Wood Science and Engineering, Luleå University of Technology, Forskargatan 1, S-93197 Skellefteå, Sweden [email: dick.sandberg@ltu.se]
[4]University of Primorska, Andrej Marušič Institute, Muzejski trg 2; SI-6000 Koper, Slovenia [email: andreja.kutnar@upr.si]
[5]InnoRenew CoE, Livade 6; SI-6310 Izola, Slovenia [email: andreja.kutnar@innorenew.eu]

Keywords: Wood modification, Europe, COST

ABSTRACT

Wood modification (chemical, thermal, impregnation) represents an assortment of innovative processes currently being adopted in the wood protection sector. Though many aspects of these treatments are known, the fundamental influence of the process on product performance, the environment, and end of life scenarios remain relatively unknown. It is essential to integrate interactive assessment of process parameters, developed product properties, and environmental impacts. To optimise modification processing to minimise environmental impacts, much more information must be gathered about all process related factors affecting the environment (VOC, energy use, end of life use, etc.). To this end, COST Action FP1407 (Understanding wood modification through an integrated scientific and environmental impact approach - ModWoodLife) was initiated in 2015, with its 4-year programme aiming to investigate modification processing and products design with emphasis on their environmental impacts. This will require analysis of the whole value chain, from forest through processing, installation, in service, end of life, second/third life (cascading) and ultimately incineration with energy recovery.

A recent task within COST FP1407 was to re-evaluate the current status of wood modification across the member countries, tasks previously undertaken within COST Actions E22 and E37 respectively and reported in several papers within several of the previous European Conferences on Wood Modification (ECWM). Whilst the early projected advances anticipated for various types of modified wood has not been as previously reported. During a COST FP1407 meeting in Florence, Italy, the national status of wood modifications in 18 different European countries was presented, and the findings will be presented herein.

INTRODUCTION

The need to treat wood to extend its service life by minimising threats from biological attack (in the form of insects, fungi, mould etc.) has long been recognised. As such, wood has been historically treated with preservatives to increase its resistance to decay caused by insect attack, micro-organisms and damage caused by marine wood-boring animals (Larsson Brelid 1998), with commercial activities since the 1830s, when sleepers and poles of railroads were pressure impregnated by a heterogeneous mixture of polycyclic aromatic hydrocarbons PAH, creosote, (Rowell 2005). Wood preservatives can be divided into two general classes: Oil type (creosote) and waterborne salts for example chromated copper arsenate (CCA) and alkaline copper quaternary ammonium ACQ (Rowell 2005). Each active ingredient which is incorporated into wood preservative formulations has its own mode of action (Eaton and Hale 1993). The toxicity of heavy metals has been widely used to fight fungal decay of wood. Some of the mechanisms of toxicity involve denaturation of proteins, inactivation of enzymes, cell membrane disruption, inhibition of respiration and inhibition of protein synthesis (Eaton and Hale 1993; Rowell 2005). However, concerns over the toxicity of traditional preservatives in use and in residuals led to the withdrawal of many of these products, to be replaced with less toxic preservatives. This also allowed an opportunity for alternative treatments to gain a market entry, among these being wood modification.

Wood modification is an alternative to conventional preservation for the protection of wood. By definition, wood modifications do not have a toxic mode of action as is the case for preservative treated wood (Hill 2006). Similarly, the modified wood should itself be non-toxic under service conditions, and there should be no release of any toxic substances during service, or at the end of service life (Hill 2006). As a result of the modification process, the wood constituents can be physically altered, and/or the wood structure can be chemically altered, such that these changes can result in more durable wood (Hill 2006) or a material with reduced hygroscopicity. There are several ways to chemically modify the wood cell wall polymers and the most abundant single site for reactivity is the hydroxyl groups (Rowell 2005). The hydroxyl groups in the wood polymers (i.e. cellulose, hemicellulose and lignin) are the most reactive sites in the wood (though there are differences in their relative reactivities). They are also responsible for the dimensional instability through their hydrogen bonding to water (Larsson Brelid 1998). Chemical modification of the wood by reacting the hydroxyl groups with a stable, covalently bounded, less hydrophilic group, leads to an increased dimensional stability (Larsson Brelid 1998).

There are or have been several examples of commercial wood modifications (with some of the original scientific publications) in recent years: thermal modification (Tjeerdsma *et al.* 1998; Sailer *et al.* 2000), furfurylation (Schneider 1995; Westin 1996; Lande *et al.* 2008), modification with DMDHEU (dimethylol dihydroxy ethylene urea) (Militz 1993) and acetylation (Militz 1991; Larsson Brelid *et al.* 2000). The role of wood modification has gained significant interest and research over recent years, as demonstrated through the European Conferences on Wood Modification (an outcome from the European Thematic Network on Wood Modification which ran between 2000-2003), and the regular sessions within the annual International Research Group on wood Protection (IRG) conferences.

WHAT IS COST?

Founded in 1971, COST – European Cooperation in Science and Technology – is the first and widest European framework for the transnational coordination of nationally funded research activities. It is based on an inter-governmental agreement and comprises currently 36 European Member Countries plus one Cooperating State, as shown in Figure 1.

Figure 1: Countries funded under the COST scheme

COST's mission is to strengthen Europe's scientific and technical research capacity by supporting cooperation and interaction between European researchers, covering from basic to applied or technological research and including research addressing issues of pre-normative nature or of particular societal importance. It anticipates and complements the activities of the EU Framework Programmes, constituting a "bridge" towards the scientific communities of COST Inclusiveness Target Countries (countries outside the original EU-15 nations shown in dark in Figure 1). It also increases the mobility of researchers across Europe and fosters the establishment of scientific excellence.

The former science organisation which was structured into nine science and technology domains has been replaced by a new organisation aiming at guaranteeing a fully open and bottom-up approach through the establishment of a single Scientific Committee. This also includes a renewed evaluation and selection procedure aiming at identifying breakthrough ideas and favouring interdisciplinary and multidisciplinary projects.

COST FP1407

The forest-based sector can become a leader in achieving the European Commission's ambitious target of reducing CO_2 emissions with innovative production technologies, reduced energy consumption, increased wood products recycling, and reuse. Apart from these undoubted environmental benefits, the use of forest products in long life products, such as built environment applications, allows for the possibility of extended storage of atmospheric carbon dioxide. Wood modification (chemical, thermal, impregnation) is an assortment of the innovative processes currently being adopted. Though many aspects of these treatments are known, the fundamental influence of the process on product performance, the environment, and end of life scenarios remain unknown. It is essential to integrate interactive assessment of process parameters, developed product properties, and environmental impacts. To optimise modification processing to minimise environmental impacts, much more information must be gathered about all process related factors affecting the environment (VOC, energy use, end of life use, etc.).

COST Action FP1407 (Understanding wood modification through an integrated scientific and environmental impact approach - ModWoodLife) will investigate modification processing and products design with emphasis on their environmental impacts. This will require analysis of the whole value chain, from forest through processing, installation, in-service, end of life, second/third life (cascading) and ultimately incineration with energy recovery. The aim of the Action can be shown as in Figure 2.

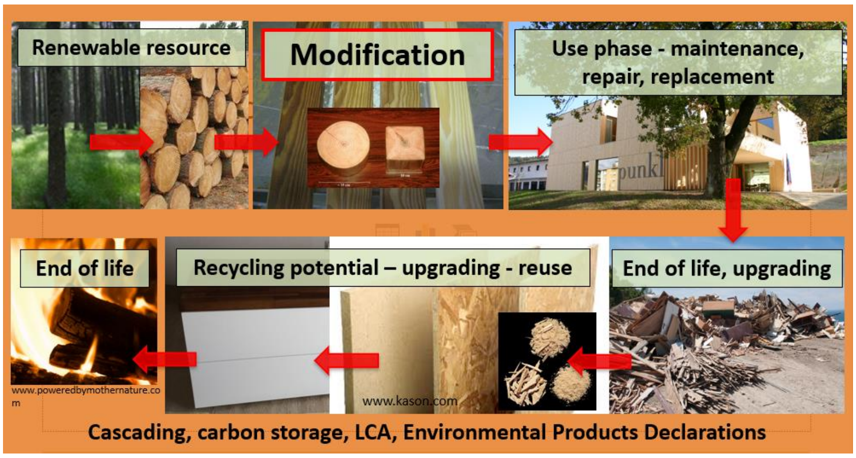

Figure 2: Schematic of the aims within COST Action FP1407

Thus, the main aim of this Action (running from 2015 to 2019 and led by the University of Primorska, Slovenia) is to characterise the relationship between modification processing, product properties, and the associated environmental impacts. This includes the development and optimisation of modified processing and quantification of the impacts of emerging treatment technologies compared to traditional processing and alternative materials to maximise sustainability and minimise environmental impacts.

WOOD MODIFICATION IN EUROPE

Since the Thematic Network of Wood Modification, where the emphasis was on the development of three processes (acetylation, thermal modification and furfurylation), there has been a steady growth in the transfer of laboratory-based studies to industry. This was clearly shown in a review by Militz (2015), where the progress of additional methods was presented (Figure 3).

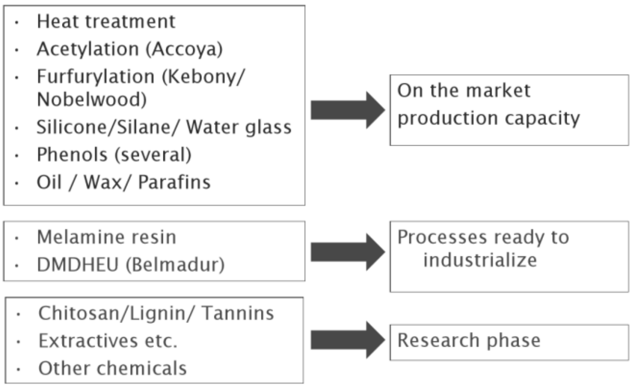

Figure 3: Overview of extent of commercialisation of modified wood processes in Europe (Militz 2015)

Overview of current production levels

In this review (Militz 2015), it was estimated that there was approximately 350,000 m^3 of modified wood produced per year, dominated by thermal modification (estimated at 300,000 m^3, of which approximately half could be assumed to be from the ThermoWood Association (Dagbro 2016)). As a part of COST Action FP1407, it was decided to review the production values across Europe, whereby each national production level was determined. Table 1 provides an overview of the types of modification being commercially produced in each country that responded to the questionnaire.

As listed within Table 1, there are a few examples of processes under development. In Belgium, there are plans to develop a new furfurylation plant in a collaboration between Kebony (Norway) and Transfurans Chemicals (Belgium) and Foreco (Netherlands), with initial productions volumes estimated at 20,000 m^3.

Country	**Acetylayion**	**Thermal modification**	**Furfuryation**	**Silicate/ Silanes**	**Resins**	**Waxes / Oils**	**Mixed anhydride**	**Thermo-hydro modification**
Belgium		++	++ (u.d.)	+ (u.d.)				
Estonia						+		
France		++					+	
Germany		++			n.a.	n.a.		
Hungary								+
Italy		+		+	+			
Macedonia		+						
Netherlands	++	++	+		n.a.			
Norway		+	++					
Poland								+
Romania		+						
Slovakia								
Slovenia		+						
Spain		+						++
Sweden		+		++				
Turkey		++						
Ukraine				n.a.				
UK	++ (u.d.)	+		+	+			

Legend: + Commercial production under 10000 m^3/year, ++ Commercial production over 10,000 m^3/year, n.a. figures not available, u.d. production under development

The development of organosilicon compounds by Dow Construction Chemicals at their R&D site at Seneffe, Belgium, based on successful results from the EU Life+ project SILEX. In the U.K., there are plans to develop new acetylation plant for producing wood chips for the manufacture of Tricoya ™. Work has already begun on the construction of a plant at Hull in a collaboration between B.P (UK), Accsys Technologies (UK/NL) through its subsidiary Tricoya Technologies Limited (TTL, UK) and Medite Europe (Ireland), which will ultimately produce 30,000 tonnes of acetylated wood chip (Figure 4). This material will help serve manufacturing rights with Medite, as well as in a new commercial venture with FINSA (Spain).

Figure 4: Breaking of soil for new acetylation plant for wood chips at Hull, UK

Table 1: Overview of responses to levels of commercialised wood modification in European countries within the COST FP1407 questionnaire

From Table 1, it can be seen that there has been a considerable increase in recent years in the range of treatments being commercially produced across Europe, and whilst production figures at these new sites remain fairly low (often around 1,000 m^3 a year), it demonstrates the desire of companies to provide local solutions to architects and specifiers.

Table 1 does not cover any input from Finland, as data was not presented at the COST FP1407 meeting. However, it is well known that Finland is the manufacturing base for ThermoWood. Recent data from the ThermoWood Association (International ThermoWood Association 2017) suggests that the group as a whole produced 193,700 m^3 in 2017

Whilst outside the scope of this study within COST FP1407, an overview of the Russian wood modification market was recently undertaken. In this (Kiseleva *et al.* 2017), the classifications of modified wood according to Russian standards were identified within four different classes (Table 2, State Standard of USSR 1980). Of these classifications, it is the Thermomechanical processing that is most common within Russia, since it includes conventional thermal modification. It was reported (Kiseleva *et al.* 2017) that there were some 20 companies producing TMT in 2010, with a maximum production capability of around 60,000 m^3. In addition, it was reported (Kiseleva *et al.* 2017) that there were enterprises active in other classifications of modified wood.

Table 2: Overview of wood modification classifications (State Standard of USSR 1980)

Modification approach	Explanation
Thermomechanical	Pressure modification of pre-heated, steamed, dried or impregnated wood with further high temperature drying and thermal modification
Chemo-mechanical	Pressure modification with preliminary or simultaneous wood plastification by ammonia or urine or impregnation with resins or lubricants and further thermal modification
Thermochemical	Impregnation with monomers, oligomers, or resins with further thermal modification in order to polymerise or polycondensate the impregnated compound in the wood structure
Chemical	Impregnation with ammonia or acetyl oxide in order to change the chemical composition of the wood
Radiation chemical	Impregnation of wood with monomers, oligomers or resins with further polymerisation of those under the influence of ionising radiation

Uses of modified wood

Modified wood has gained market entry across a range of Use Classes, depending on the levels of treatment and how they alter the durability and moisture exclusion levels of the treated material. Some examples of these modified wood in Use Classes are given in Figure 5.

Use Class 1 | Use Class 2 | Use Class 3 | Use Class 4

Figure 5: Examples of modified wood in Use Classes 1-4

The ease of modification, and in particular thermal modification has occurred as a result of several equipment manufacturers diversifying from conventional kiln and impregnation vessel manufacturing to produce small scale reactors, such as that produced by ISVE in Italy, who have sold several reactors internationally in addition to three being used within Italy for local production (Figure 6).

Figure 6: Example of a small scale thermal modification reactor (IVSE, Italy)

CONCLUSIONS

The use of modified wood continues to increase across Europe. In addition to the three main wood modification processes (acetylation, thermal modification, furfurylation), there has been a recent increase in the number of alternative processes being commercialised. In addition, there has been an expansion of the number of companies producing thermally modified wood, particularly for local use in a given country. The findings of COST FP1407 appear to show similar volumes to those estimated in 2015 (Militz 2015), particularly when taking on board the latest figures for the ThermoWood Association. The European production levels may be further increased through the inclusion of Russian production volumes, even though these figures are now several years old. This continued demand for modified wood is despite the slow-down within the construction sector. This suggests that modified wood is gaining more favour with architects, specifiers and end-users, which suggests a continued success for modified wood across Europe.

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What is Wrong with Wood Modification in the U.S.?

Jeffrey J. Morrell[1]

[1]Australian Centre for Timber Durability and Design Life, Brisbane [email: jmorrell@usc.edu.au]

Keywords: acetylation, termite attack, thermal modification

ABSTRACT

Many wood modification processes were originally developed in the United States, but modified wood products are relatively rarely used there. This paper examines the reasons why modified wood products are infrequent and then outlines potential opportunities for their use in the United States.

INTRODUCTION

Wood is one of the few truly renewable structural materials on the planet and will become increasingly important as we eventually emerge from the petroleum age. At the same time, wood is a biological material prone to degradation by both biotic and abiotic agents. Although they did not understand the underlying nature of wood deterioration, humans have long employed various methods for preventing or delaying the process. The most important of these were keeping the wood dry and using timbers with durable heartwoods. These two tenets of using wood remain the prevalent methods for employing wood in various structures; however, there are many applications where the wood cannot be kept dry or where sufficient supplies of durable heartwood species are lacking.

The development of effective chemicals for limiting biological attack coupled with methods for delivering them into the wood ushered in a golden age of wood protection (Graham 1973). Creosote and, later synthetic systems, became widely used in a variety of applications in an era where broadly toxic preservatives were more readily accepted by the general public. Nowhere was preservative treated wood more widely accepted than in the United States, where the need for durable exterior construction materials for outdoor living features such as decks and fences created an ever-growing demand for this material. The most common preservative for residential material was chromated copper arsenate, while creosote and pentachlorophenol dominated industrial markets. The growing residential markets coupled with existing industrial uses led to the U.S. representing over 60 % of the global treated wood use.

The 1960's witnessed growing concerns about pesticides that eventually led to examinations of all pesticide used. Eventually, restrictions were placed on the use of many commonly used wood preservatives. The approaches taken to these concerns and restrictions differed markedly from Europe where many registrations were cancelled and some governments banned the use of some preservatives.
The review will begin with a quick discussion about the origins of wood modification in North America, outline the basic differences between standardization in Europe and NA, and then discuss how these affect the current state of modified woods. It will discuss this from a U.S. perspective. I will use the term Americans and the United States (U.S.) interchangeably. Clearly, America also refers to citizens of other countries in North and South America, but, for the purposes of this paper, it will refer only to the U.S.

It is somewhat ironic to attend a wood modification meeting in Europe, which has become the recognized leader in this field when one considers that the United States was source of many of modification methods currently employed (Hill 2006). Early work by Alfred Stamm and others at the U.S. Forest Products Laboratory examined thermal modification, resin impregnation, acetylation, and a host of other non-biocidal approaches to wood protection (Seborg *et al.* 1953, Stamm 1956, 1959, Stamm and Seborg 1943, Stamm *et al.* 1946, Tarkow 1966, Tarkow *et al.* 1946). Rowell later tried to move this work forward (Rowell 2005, 2006, Kumar 2006). Yet, decades after Stamm's pioneering work in this area and Rowell's efforts, modified wood products represent only a tiny fraction of the U.S. durable wood market. Why? There have been recent moves to examine explore modified wood in the U.S. (Aro *et al.* 2014, Barnes *et al* 2016), but a failed effort by Eastman Chemicals to bring wide-scale use of acetylated wood to the U.S. illustrates the difficulty of introducing new technologies.

Understanding the barriers to widespread adoption can be useful for determining the potential for these products in the U.S. market. We can categorize these barriers as specification-based, consumer based or market-based. We will discuss each separately and then integrate the topics to outline possible pathways forward for modified wood in North America.

Specification Based Limits

First, it is important to understand that Americans have a strong dislike for government regulation and will sometimes go to extraordinary lengths to self-regulate to avoid what is viewed as government interference. The Andersonis just one such example of this approach. Found in 1904 as the Wood Preservers Association, its intent was industrial self-regulation (probably with a touch of establishing monopolies and fixing prices, both poplar in the early part of the 20th Century). The AWPA sets voluntary consensus standards based upon the activities of those who produce and use treated wood. The U.S. building codes adopt the AWPA Standards, which makes them mandatory for structural applications but even these codes can be modified for local situations.

At the same time, government does become involved with treated wood, but only through chemicals used for this purpose not the resulting products. The U.S. Environmental Protection Agency by law, regulates all materials that make pesticidal claims under the Federal Insecticide Fungicide and Rodenticide Act (FIFRA). Although chemical producers may disagree, the process tends to work in a consultative fashion with considerable interaction between regulators and proponents. As in Europe, proponents submit data supporting their registration, but the process is fairly interactive. As a result, while chemicals are sometimes withdrawn from markets because of safety concerns, they are rarely banned by the government. This process creates a more interactive system where wood preservatives are registered by the EPA based upon toxicity data while the marketplace primarily drives whether a given system is actually used. This sharply reduces pressure to use substitute systems as long as the public is satisfied with the status quo. This differs substantially from Europe where there is more government oversight and control.

One major factor limiting widespread use of modified woods in the U.S. is the method by which materials are standardized. As mentioned earlier, the AWPA is the primary standards writing body for durable woods (including preservative treatments) in the U.S. AWPA is a voluntary, consensus standards writing body, although its standards are incorporated into required building codes. There is a second process for use of durable woods through the International Code Council Evaluation Service (ICC-ES), but it essentially uses the AWPA Evaluation Standards for their approval process. In both cases, there are protocols for standardizing chemicals and treatment processes that list the tests required for different Hazard Classes or Use Categories (AWPA, 2017). The key features for all of these requirements are the need for a minimum of 3 years of field data, the need to evaluate resistance to termite attack and the availability of relatively rapid methods for assessing treatment quality. Laboratory data, while also required, is not the primary factor in the decision to standardize a system. Even field data; however, can be difficult to transfer between countries. For example, Metsa-Kortelainen and Viitanen (2017) showed that in ground performance of modified scots pine and Norway spruce was better than similar non-modified wood over a 6 year period; however, the rates of decay were far slower than those found in many parts of the U.S. and no termites were present at the test site. As noted later, the presence of termites across nearly all of the U.S. necessitate considering these insects in the development of new materials.

Some of the data required to demonstrate performance can originate from Europe; however, there are clearly differences in test methods that will require the use of U.S. methods and field exposures. For example, Vidrine *et al.* (2007) found that thermally modified ponderosa pine and yellow poplar performed poorly in U.S. soil block tests. While this does not necessarily mean that all tests must be performed in the U.S., differences in decay risk require a modified approach to standardization (AWPA, 2017).

The most difficult U.S. requirement for most proponents of modified wood systems to meet is the requirement that any treatment must be verifiable any time after treatment. This becomes problematic when there is no specific analysable component in a system. Acetylated wood proponents appear to have met this requirement through determination of acetyl content but other systems have struggled. For example, there is no system for determining the degree of thermal modification without resorting to either a record keeping/process approach that is not verifiable or sophisticated analytical tools not available in most treatment facilities. Record keeping does not allow an inspector on a job site to determine if material meets a quality standard. The U.S. is a litigious society and material failures often end up in lawsuits among affected parties. The inability to assess treatment quality poses a major challenge in these cases. The availability of methods for assessing treatment quality also helps protect producers who can show that materials were properly prepared.

The AWPA also requires that there be some way to visually assess treatment quality to a given depth in the wood (i.e. penetration) colour changes or some form of chemical indicator. This requirement can be equally challenging to proponents, although there is some potential for assessing colour changes for the thermal processes. The issue of assessing quality control is especially thorny with thermal modification because of the wide array of methods employed in this process and the potential to use these processes to produce differing degrees of thermal modification (Esteves and Pereira 2009).

Proponents of modified woods have generally been frustrated by the U.S. standardization requirements. While standards committees have discussed methods for accommodating modified wood systems into their standards, no consensus has been reached and it appears unlikely that the AWPA will modify its requirements to accommodate process-oriented quality control (i.e. record keeping) in place of actual sampling of production. At present, that leaves many modified wood products with no verifiable assay procedures for assessing quality. This is clearly a limiting factor for widespread adoption of modified wood technologies and there is a critical need for development of new methods for assessing treatment quality.

Consumer Limits

A major factor affecting the American market is cost. While many consumers say they will buy less toxic materials, their actual purchasing behaviour can differ markedly. For example, Anderson and Hansen (2004) examined purchasing behaviour for Forestry Stewardship Council certified plywood and found that price differences as small as 2 % per sheet between certified and non-certified materials were enough to alter consumer behaviour. While there is a small segment of the population that will pay more for materials perceived as more environmentally friendly, most consumers remain price-driven as evidenced by the preponderance of large lumber retailers or so-called big box stores in the U.S. that drive prices down.

Another factor limiting widespread use of modified woods in the U.S. is the presence of active termite attack in most areas of the country. While some of the modified wood product such as acetylation, furfurylation and resin impregnation have performed well against termites, others such as thermal modification, have not. Termites are absent from a very tiny portion of the northern part of the U.S., but are found in parts of every State in the country. This makes it hard to market a non-termite resistant product.

The final consumer factor is a combination of level of knowledge about durable materials, ability to distinguish between valid and inaccurate market claims, and the risk of litigation should materials not perform to expectations. Those entering the market must have a long-term plan for market development that clearly defines the limits of their products to avoid creating unrealistic consumer expectations. Failure to define the performance limits will ultimately lead to performance issues and costly litigation.

Market Factors

The final important factor in the U.S. relates to our wood use patterns in the market. Wood is the dominant material for residential construction and, to the outsider, the U.S. looks like a market with tremendous potential for use of durable woods; however, nearly all of the wood is employed in dry-use applications where the risk of decay is minimal. Beetles, although sometimes present in structures, are not a major problem. As a result, most materials used in buildings do not require protection. The only durable material used in most buildings is the sill plate that separates the foundation from the rest of the house above. Depending on the locality, this can be either naturally durable or preservative treated. The remainder of the structure is constructed using non-treated wood.

Exterior cladding could be a market for durable materials. For decades, western redcedar was a preferred siding material, but cost and availability reduced the use of this material. Substitute composite products performed poorly in this application and the resulting litigation led to a shift to wood/cement siding products. Modified wood products might gain a share of this market provided they could fall between the lower end siding products and the higher end naturally durable cedars. This would primarily be a marketing effort since wood already has a history of use in this application and the data requirements for market entry are minimal.

The remaining applications for durable materials in the U.S. are in outdoor uses such as fences, decking, and railing. These applications do present some opportunity, but the market is already filled with competing products including naturally durable timbers, wood/plastic composites, and traditional preservative treated wood.

Fencing is generally a low value market. Durable woods such as cedar and treated wood dominate this market, although plastic fencing has gained some market share. The unwillingness of consumers to pay a premium for fencing is illustrated by the presence of non-durable products sprayed with a surface pigment to make them look like naturally durable materials. Consumers have little knowledge about performance attributes that might lead them to delineate between products.

Decking has the greatest market potential for some modified wood products, but the risk of termite attack must be considered in this effort. Termites can and do attack wood above ground in many parts of the U.S. Durable timbers such as Ipé, redwood and western redcedar find regional usage in decking, but are far more costly than treated wood products. Redwood and western redcedar are traditionally more heavily used closer to the sources in the Western U.S. Ipé is used in higher value homes, but there have been general questions about the sustainability of tropical timbers. The use of wood/plastic composites has grown over the past decade although it still only represents 20-25 % of the overall deck market. While high costs continue to limit use to more expensive homes, WPC costs are decreasing to the point where they are similar to those for naturally durable heartwoods such as western redcedar. From a European perspective, the market now occupied by WPC ‘s would be the most likely target market for modified wood products. A 2006 survey of consumer attitudes indicated that naturally durable woods and WPCs were more favorably viewed than treated wood (Fell *et al* 2006). This suggests that consumers might be willing to pay slightly more for a product with perceived environmental benefits, although perhaps not as much as they might for a tropical timber. This creates possible intermediate niches for modified woods that merit exploration.

The Future

It is always hard to predict the future but that never stops one from attempting it. It is clear that there is a public desire to use less toxic materials, although it is also clear that most U.S. consumers really do not know exactly what that means. Extraordinary performance claims of effectiveness about some products do not help this situation. At the same time, the presence of termites in most of the country, the higher costs of modified wood products, and U.S. standardization requirements all make it more difficult for many modified wood products to achieve high market penetration. It is also unlikely that government regulations regarding preservatives will change dramatically. Despite these limitations, some products, most notably acetylated wood, are finding market niches and being incorporated into the national standards. This process has been slow, and it requires making sure that materials are fit for purpose, avoiding extreme performance claims and identifying markets where modified wood has perceived consumer value.

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SESSION TWO

Commercial and Market Opportunities for Modified Wood

New Standards for Approval of Modified Wood within the Nordic Wood Preservation Council (NWPC)

Niels Morsing[1], Søren Bang-Achton[1], Emil Engelund Thybring[2] and Morten Klamer[1]

[1]Danish Technological Institute, Wood and Biomaterials, Gregersensvej 3, DK-2630 Taastrup,
[email: nmo@dti.dk]
[2]University of Copenhagen, Department of Geosciences and Natural Resource Management, Forest, Nature and Biomass, Rolighedsvej 23, DK-1958 Frederiksberg C [email: eet@ign.ku.dk]

Keywords: Modified wood, NTR, NWPC, Quality assurance, Standardization

ABSTRACT

In the Nordic countries, there is a long tradition for quality labelling of preservative treated wood. Until now the labelling has been restricted to pine and other easy to treat wood species, but with the introduction of a new set of standards it is now possible to obtain the Nordic Wood Preservation Council's (NWPC) quality labelling also for modified wood.

In this paper, we will introduce the background and criteria for approval according to NWPC for modified wood.

INTRODUCTION

The use of different modification techniques can be defined as *a chemical, biological or physical treatment of the wood material, resulting in an improvement of the properties in service. The modified wood must be non-toxic in service and no leaching of toxic substances is allowed in use, at disposal or when recycled* (Hill 2006). Different techniques such as furfurylation, acetylation and heat treatment, have been introduced with only limited commercial success even though they may demonstrate a good degree of protection. This is mainly because the modified wood is quite expensive compared to traditional treated wood and may demand specialized treatment facilities. However, since the introduction of the Biocidal Products Regulation (BPR) in Europe there has been a growing interest for protecting wood from degradation without the use of biocides. Modified wood possesses different abilities than traditional treated wood, so, there is a need to define criteria on how to evaluate the efficacy of the different treatments.

The moisture content of wood has often been linked to durability, *i.e.* resistance to biodegradation (Ammer 1963, Stienen *et al.* 2014, Meyer & Brischke 2015). For instance, in reviewing moisture relations of six different types of wood modifications, Thybring (2013) found a common threshold moisture content across the various modifications which hindered fungal decay in the modified materials. The physical mechanism behind decay resistance for materials with reduced moisture uptake might derive from limited diffusivity of ions (Zelinka *et al.* 2016). Thus, brown-rot fungi which are the most widespread and devastating agents for decay in wood structures (Duncan & Lombard 1965, Viitanen & Ritschkoff 1991, Alfredsen *et al.* 2005, Schmidt 2007) use small chelators for diffusing iron ions into wood cell walls and making them react with hydrogen peroxide secreted by the fungi (Goodell *et al.* 1997, Xu & Goodell 2001, Arantes & Milagres 2007, Hastrup *et al.* 2013, Ringman *et al.* 2014). Hereby, highly reactive free radicals disrupt chemical bonds of the cell wall constituents.

By limiting the cell wall moisture content, the formation of a continuous network (percolation) of absorbed water in which ions and other solutes might be prevented. This hypothesis is based on the observation by Zelinka *et al.* (2015) that diffusion of ions within cell walls is completely halted if the cell wall moisture is too low.

As the moisture content varies with climatic conditions, Thybring (2013) linked decay resistance of modified wood with the moisture exclusion efficiency (MEE), i.e. the relative moisture reduction in modified wood compared to untreated controls exposed to similar environmental conditions. Overall an MEE of 40 % was found to provide decay resistance across the various modifications.

The NWPC standards introduces MEE as a new parameter to evaluate and control the degree of modification and indirectly the efficacy of the product to prevent fungal degradation.

REQUIREMENTS

The conditions are in principle based on EN 599-1 introducing additional requirements with respect to the mode of action of the modified wood. The standard is applicable to industrial treatment of any wood species suitable for the treatment if the requirements are fulfilled:

- Modification of wood involving a chemical, biological or physical treatment of the wood material, resulting in an improvement of biological durability in service. The method used must not involve a product that is listed as an active ingredient (biocide) in the BPR. No emission of toxic substances from the wood listed in *list of approved active substances by ECHA* is allowed in use, at disposal or when recycled.

Examples on physical treatments could be *e.g.* thermally modified wood, steam treated wood and densified wood and chemical treatments could be chemical agents that are either filling the lumen and/or cell wall or reacting with the cell wall components.

The modification procedure, *i.e.* both possible agents and the process of modification, must be described in full detail as well as the possible mode of action when applying for an approval. In case of chemical modification with penetrating processes, the following applies:

The state of delivery, *e.g.* paste, granulate or liquid, and the complete formulation of the modifying agent shall be given. The ingredients shall be stated by empirical formula, CAS and EINECS number if applicable and percentage (m/m). If additives are used, these shall be stated by type.

The efficacy of the modified wood is tested according the requirements listed in Table 1.

Table 1: Minimum requirements for testing expressed as MLP: Mass Loss Percentage after exposure to biological attack.

Test Methods:	**NWPC Wood Preservation class**			
	B mod	**AB mod**	**A mod**	**M mod**
EN 73 + EN 15083-1 without *Coriolus versicolor*	MLP<10%	MLP<10%		
EN 73 + EN 15083-1 with *Coriolus versicolor*			MLP<5%	MLP<5%
EN 84 + EN 15083-1 without *Coriolus versicolor*	MLP<10%	MLP<10%		
EN 84 + EN 15083-1 with *Coriolus versicolor*			MLP<5%	MLP<5%
EN 330 (the untreated reference samples shall have reached the mean rating 2 of severe decay)	+	+		
CEN/TS 12037 (the untreated reference samples of Scots pine sapwood shall have reached the median rating 3 of severe decay)		+		
EN 73 + EN 15083-2			+	+
EN 84 + EN 15083-2			+	+
EN 252 (≥ 5 years)*			+	
EN 275 (≥ 5 years, one Nordic test site)				+
MEE (85% RH) after ageing according to EN 73	>40%	>40%		
MEE (85% RH) after ageing according to EN 84			>40%	>40%

**At least three relevant test sites including two in Nordic countries*

The mode of action for modified wood is most often based on moisture exclusion or in other words, a reduced moisture content in the modified wood compared to untreated wood. MEE is calculated as the relationship between the difference in equilibrium moisture content (EMC), between untreated (EMC_u) and modified wood (EMC_m) and the moisture content of the untreated wood (EMC_u). The EMC_m must be adjusted for the weight percent gain (WPG) after the modification treatment of the wood. The range of RH must include 85% and contain at least four measuring points on the sorption isotherm.

$$MEE\ (85\%\ RH) = \frac{EMC_u(85\%\ RH) - (1 + WPG/100) \cdot EMC_m(85\%\ RH)}{EMC_u(85\%\ RH)} \qquad (1)$$

MEE must be above 40%.

Reference specimens should preferably be *Pinus sylvestris* sapwood for testing modified wood based on softwood and *Fagus sylvatica* for testing material based on hardwood.

The set of standards for modified wood follow the system for NWPC approval. That is a Document 1 covering the general aspects, a Document 2 describing the criteria for the supplier of the technique/chemicals needed and a Document 3 giving the rules for third party control of treatment plant and production (NWPC 2017a-c).

In Table 2 the correlation between NWPC classes and the CEN standardisation system is shown and in Table 3 is shown examples of different end-uses.

Table 2: NWPC wood preservation classes M, A, AB, B, GRAN*, GW*, HW*, HC*, AB mod, A mod, M mod, B mod in relation to EN 351-1 and EN 335-1.

Penetration class according to EN 351-1		**Use classes 1 to 5 according to EN 335-1 and their relation to the wood protection classes**				
Class	**Penetration Requirement**	**UC 1**	**UC 2**	**UC 3**	**UC 4**	**UC 5**
NP 1	None			GRAN GW HW HC		
NP 2	Min 3 mm lateral into sapwood					
NP 3	Min 6 mm lateral into sapwood			B B mod		
NP 4	Min 25 mm					
NP 5	Full sapwood			AB AB mod	A A mod A Pole	M M mod
NP 6	Full sapwood + 6 mm into heartwood					

** GRAN (Spruce), GW (spruce for window), HW (heartwood for window), HC (heartwood cladding)*

Table 3: Examples of end-uses for industrial protected wood.

Use class according to EN 335-1	**Service conditions**	**Example**	**Recommended wood preservation class according to NWPC**
1	Interior timbers in dry conditions.	Furniture, interior cladding	1)
2	Wood above ground and under cover and fully protected from the weather, but where high environmental humidity can lead to occasional but not persistent wetting.	Roof trusses, exterior timbers under cover	1)
3	Wood above ground and either continually exposed to the weather or subject to frequent wetting; where it is relatively easy to replace damaged components and where the consequences of failure will be moderate.	3.1 External joinery, such as windows, doors *etc.* 3.2 External cladding, garden timbers	B, GW, HW AB, GRAN, HC, AB mod, B mod
4	Wood in contact with the ground or fresh water or severely exposed to the weather; or if a wood component is inaccessible, or where the consequences of failure will be particularly serious.	Transmission poles, railway sleepers, fence posts, bridges	A, A mod
5	Wood constructions in sea water2) and constructions subject to extreme conditions or where there are special durability and strength requirements.	Wharf timbers, jetties, piles	M, M mod
1) Preservative-treated wood normally not necessary to use in these use classes 2) Salinity > 0.6%			

Besides the requirements in Table 1 the application shall contain documented results of the treatability properties and stability in use and storage of the modifying agent for chemical treatments. This must be performed at an independent institute as specified in NWPC Document 2 (2017b).

THIRD PARTY CONTROL

The NWPC Board approves quality control bodies to carry out quality control of modified wood according to NWPC Document 3 Part 4 (2017c). Quality control bodies shall have sufficient expertise and logistics in handling third party control related to the wood industry.

The aim of the third-party control is to ensure that the factory production control inspections is carried out and to check that the quality of the modified wood complies with the requirements in the NWPC Documents.

The third-party control shall be carried out through at least two unannounced visits during one calendar year.

The following points must be covered at each inspection:

- check that factory production control and treatment records are carried out continuously according to given instructions
- check the plant's equipment for factory production control and the wood moisture content
- take a sample of the modifying agent for chemical and/or physical analysis if applicable
- take random samples from the treated wood for analysis of the penetration, WPG, colour, weight loss, or other relevant parameters related to the treatment intensity.
- check that updated instructions are available
- check that requirements for delivery and marking are fulfilled
- check that any particular national requirements are fulfilled.

The inspector cannot ask for information regarding conditions that are not specified in the NWPC documents.

After the inspection, a report with the results of the analyses carried out, as well as any observations of importance, will be sent to the producer.

SANCTIONS

For all NWPC standards the same set of rules for sanctions apply (NWPC 2017 c) that may result in withdrawal of the right to label wood with the NWPC quality label.

CONCLUSION

With the introduction of this new set of standards NWPC now covers a wide range of wooden commodities and techniques for wood protection as shown in Table 4 below.

Table 4: Overview of NWPC standards

Part of NWPC document	Commodities	Technique covered
1	Pine species and other easy to treat species	Penetrating processes (*e.g.* vac-pressure, Dobb vac)
2	Spruce	
3	Heartwood	Superficial treatments
4	Modified wood	Chemical modification Heat treatment

The approval scheme is operated by the NWPC and a certificate confirms the approval of the treated wood product. The approval is valid in Denmark, Finland, Norway, Iceland and Sweden.

DISCLAIMER

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Kebony Clear – Produced in Belgium

Per Brynildsen[1]; Omar Roels[2], Bruno Van den Branden[2]

[1] Kebony AS, Havnevegen 35, 3739 Skien, Norway [email: pb@kebony.com]
[2] Kebony Belgium NV, Ketenislaan 2, 9130 Kallo, Belgium

Keywords: Kebony wood, Business Development, Engineering, Plant design, Risk management

ABSTRACT

Since 2014, the sales of Kebony® wood products have taken full capacity from Kebony's first factory in Norway. Consequently, the owners of Kebony initiated both an expansion of the Norwegian factory, and the construction of a new factory close to Kebony's main European markets. This paper will discuss the main factors in planning, designing and constructing a new Kebony factory in Belgium, and the selection of working models through those processes. Factors like site selection, facilitation by local and national authorities, regulatory framework and project execution will be described. Finally, the Kebony product range produced in the new factory will be presented with its main product properties and technical and environmental credentials.

INTRODUCTION

Background

Till this year Kebony operated with one production plant, located in Skien Norway. Already in 2014, the capacity of this plant was out-run by demand, and Kebony's owners and management started planning for new production capacity. Since the fastest growth in demand is in continental Europe, it was decided to find a site for a new factory in Germany, The Netherlands or Belgium.

Kebony mainly sells its radiata pine based decking and cladding products in the European market. These products are based on clear grade sapwood of radiata pine, with the Kebony treatment being through the cross section of the boards.

Future needs

To meet growth in the main European market, the new factory was to be designed for production of radiata pine based products, Kebony® Clear. This decision has implications for choice of equipment and some design choices for the new factory.

INITIAL PLANNING – SETTING THE REQUIREMENTS

Design Basis

In any project the *design basis* is a crucial starting point. As stated by Towler and Sinnot (Towler and Sinnot 2008), the design basis is a formal statement of the overall requirements that should be met, or the problem that should be solved. For the Kebony Belgium project the design basis was stated as a plant capable of producing more than 20 000 cubic meters of sawn Kebony® Clear products per year.

Facilitation by Local and National Authorities

Contact with national and local authorities is crucial, from an early stage in the site selection process. Such public agencies will offer a lot of help in finding available sites and establishing contacts with local property developers, property sellers, contractors, industrial partners etc. In Kebony's case very valuable assistance was received from national trade and investment agencies in Germany (German Trade and Invest), the Netherlands (Netherlands Foreign Investment Agency) and Belgium (business.belgium.be). Typically, the national agencies will provide examples of opportunities, contacts and general information about different regions, and in the following instance the regional investment agencies will step in and arrange more detailed overviews, visits and further contacts to financing institutions, regulatory agencies, developers, land-owners and other businesses that are willing to share experiences.

In Flanders the agency is the Flanders Investment and Trade (Flanders Investment and Trade 2017).

Site selection

There are of course many factors that must be evaluated when selecting a site. Some are obvious, and some are easily overlooked. The tangible factors listed below; location, access to utilities and logistics, cost levels, type of property, general infrastructure and financial incentives are measurable in straightforward ways, and can be ranked quite easily. However, there are less tangible factors that are as important: Work culture, education quality, skilled workforce availability and cultural compatibility with the home organisation can determine the success of the project.

And last, but not least, it should be easy to reach the site from the home location, since there will be lots of travelling and exchange of personnel between the sites.

Location

The first decision is whether the location should be geographically close to the main markets or close to the main raw material sources. In Kebony's case it was decided that the new plant should serve our main European markets, and would need to be located in Germany, France, Belgium or the Netherlands.

Utilities

The Kebony process requires steam - mainly for heating the drying kilns, and utilities like water, electricity, waste handling, communication networks and easy logistics. By tying into existing nearby networks of for example steam or wastewater handling, own investments can be saved. The infrastructure of a site is thus an important criterion in the selection process.

Type of property

Another crucial decision is whether to build everything new from scratch, or take over an existing industrial building. The latter alternative may be lower on investment needs, but only if a highly suitable building can be found, which will be hard in most cases. Also the shape and size of such a building should fit for a logic product flow in production.

The whole process from initial learning about various regions to a decision, including site survey visits, discussions with property developers and financiers will take many months. In Kebony's case it took half a year to decide on the country, and another half year to finally decide the exact site.

Finally, a site with the following advantages was selected:

- Geographic region preferred by one of Kebony's major shareholders
- A vacant plot of land of suitable size, rented on concession from public authorities, with highly competitive cost for land lease. The land was un-used, so a suitable building had to be built from new
- Good industrial infrastructure, inside a developed industrial park
- Host company offering facility services like fire department, access control, site security, medical support, parking
- Utilities and energy – steam, waste water treatment, electricity, compressed/instrument air, nitrogen, plant & fire water and sewage supplied by host company
- Close proximity to major port, motor roads and rail networks
- Easily reachable from both of Kebony's Norwegian locations

In conclusion, the chosen location was in the Antwerp harbour area "Waaslandhaven-noord", inside the Scheldt Chemical and Industrial Park run by the Lanxess chemical company.

THE PROJECT

From Process Design Package to Basic Engineering and Detailed Engineering

When the production process is well developed and documented, it is time to collect all that information in a Process Design Package, or PDP. In Kebony's case, the PDP was created early on for a scenario well suited to the design basis of the Belgian project. The PDP was based on Kebony's Norwegian production plant and continued process improvements, and compiled using a Norwegian local engineering firm. Having a comprehensive, though not site-specific, PDP is very valuable when a specific project is initiated, as it is a fundament for further basic and detailed engineering.

The basic engineering, which in Kebony's case was an adaption and further development of the PDP to fit the selected site, local authority requirements and design basis, was used to specify the main designs for the buildings, surrounding area, ancillary systems and utility requirements, process design with main equipment specifications and piping and instrumentation, as well as high-level design of control systems, storage area, tank capacities etc. The basic engineering package then allowed an total investment cost estimate at the accuracy level of +/- 20%, which normally is sufficient for the owner to decide whether the project should be carried forward or not.

Choice of partners and contractual models

Although Kebony, as the project owner, has its own technology organisation, these resources are too scarce to take on the execution of a project of this magnitude. Kebony chose to engage external engineering contractors for basic engineering, detailed engineering, procurement and construction management..

The first contract to be awarded was the basic engineering contract, which would form a basis for equipment, building, piping, electrical &instrumentation, automation as well as ancillary IT system contracts. The basic engineering package also contains investment cost estimates at the +/- 20% level, enabling Kebony to make an investment budget for the whole project and arrange project funding.

After completion of the basic engineering and investment budget, and the decision to proceed by the owners, there are two main contract principles for detailed engineering and the execution of the main project:

In *lump-sum projects* the main contractor is paid for the complete finished plant at the end of the project. He does the detailed design, orders materials, manages all sub-contractors during construction and delivers all this for the whole project at a fixed price. Such lump sum models entail a relatively large risk premium and therefore come at a certain price. Although the risk of unforeseen factors is low for the owner, the owner will on the other hand have limited influence on many design and procurement solutions, and by that the total quality of the plant.

An alternative is reimbursable contracts, where the contractors are paid successively on hours and materials spent to manage the project, or parts of the project, on the owner's behalf. In such contracts, most risks associated with unforeseen changes and events are normally shifted to the owners, meaning that active and close management by the owner himself is a must. This reimbursable contract type allows the owner to adjust the plans during the execution period and finally reach a better quality end product compared to a lump-sum contracting strategy. Reimbursable contracts are also known for a fast awarding process which allows contractors to start earlier which should have a positive impact on the overall schedule. A con is that there is less control on the final contract cost. The differences between the main contract forms are very well summed up by Loots and Henchie (Loots and Henchie 2007).

Kebony combined both lump-sum and reimbursable contract models, in the following structure: A reimbursable engineering, procurement and construction management contract was entered with the main engineering partner – in this the same firm as had been used for the basic engineering. Under this EPCM contract, the engineering firm was contracted to manage, on Kebony's behalf, all engineering, procurement and construction activities in the project. The strategy that was pursued in this collaboration was to enter specific lump sum contracts with sub-contractors and equipment vendors. For example, the civil/structural and architectural contract was one contract at a fixed price. Likewise, there were lump-sum contracts for tanks, pipeworks, electrical and instrumentation installations and the main equipment / package units. This contractual structure demands very active and vigilant management from both owner and EPCM partner, and a daily seamless collaboration between the two organisations for the duration of the project.

Project Execution and Resource Allocation

The resource requirements from Kebony, the project owner, would vary through the various phases of the project.

In the design phase, Kebony's own process engineers were heavily involved with the engineering partner to correct and approve design solutions as they took shape, package by package. This is in interactive and iterative process involving not only engineering staff, but also operational staff and equipment vendors. Approval of a wrong or sub-optimal design may cause significant change costs and delays in later project stages, and should be avoided as far as possible. So, time and resources spent on design can easily save larger costs and time down the road. On the other hand, it is often hard for operations managers to set aside sufficient time for a good in-depth understanding and providing input to designs and specifications. This resource dilemma, especially for small organisations, should not be underestimated, and how it is dealt with in practice may mean significant schedule or budget gains, or costs, in the long run.

Prior to awarding contracts, the correct pre-selection of contractors and vendors based on the contract scope and contractors' expertise will be required, and is crucial for project success.

When the design solutions are established, the next phase contains procurement and construction activities. Even here internal resources are heavily involved in quality assurance of bid documentation, offers from vendors and approval of procurement orders. There may also be issues coming up during construction activities that will require engagement and decisions by owner's staff.

When the design solutions are established, the next phase contains procurement and construction activities. Even here internal resources are heavily involved in quality assurance of bid documentation, offers from vendors and approval of procurement orders. There may also be issues coming up during construction activities that will require engagement and decisions by owner's staff. Finished packages are checked on completeness and quality before mechanical completion is reached

After mechanical completion, the owner team will be engaged in commissioning of the various systems and equipment packages. This phase involves a lot of preparation (organisation, design of commissioning protocols and procedures) and requires participation both from owner's technical staff and operational staff. The actual testing and documentation during the commissioning phase requires a well aligned and prepared team, and will proceed successively till all packages are approved by the owner. At this stage the whole project is taken over by the owner, and following a successful commissioning the plant is ready for start-up.

In Kebony's case, a core team of six engineers did the dominant part of the owner's input to the whole project, while Fluor Engineering, Antwerp, was the EPCM partner managing all sub-contractors and vendors. Fluor also did the basic and detailed engineering, cost estimates, cost and schedule controls and periodic reporting.

Risk Handling and "Unknown unknowns"

There are always risks with a project, and awareness and preparation of risk handling procedures and efforts are vital for a successful execution and conclusion.

Important risk factors and risk alleviation measures:

<u>Is the project schedule driven or budget driven?</u>

It is very difficult to prioritise both schedule progress and budget discipline, although any owner will tell that both are top priority. In Kebony's project we had to stay on the project overall budget, which in some cases affected progress negatively. Ultimately, it is up to the owner to decide whether budget or time is the most important constraint in a project, but the earlier it is decided the better, since this decision affects many other decisions in the project

<u>Resources and competence</u>

A wood modification small or medium sized enterprise cannot be expected to have a large project department used to building factories in different parts of the world. However, in Kebony a small but highly skilled technology department has been built up, with the aim to support projects. Furthermore, after site selection Kebony decided that key staff for the new site should be hired as soon as possible. Consequently, almost two years ahead of start-up of the new factory the Kebony Belgium site manager and the project manager were recruited. Both are highly experienced in operations and engineering respectively, and have played a crucial role in contract negotiations and in managing the project.

Unforeseen changes in scope and content of the project

For adherence to the budget and time schedule it is crucial that the overall layout and design of the plant is decided as early as possible, and that all stakeholders are aware of the "need to have" versus the "nice to have" priorities that are baked into the project. A close follow up on “nice to have"s is required to avoid budget overruns and schedule impact because this could jeopardize the project. Every scope change that is added after the basic engineering phase will cost money and time. So, proper involvement of the key operational users, and anchoring of selected solutions, with the operational teams have to be done at an early stage of the project. Such quality assurance, involving users, project design team and contractors consists of iterative processes, and will take time. But, attention to this will reduce the risks of later changes and modifications.

Missing or delayed regulatory permits

Neither construction, nor subsequent start-up and production, can be done without the required approvals and permits from the authorities. In Belgium this entails the Environmental Permit and a Building permit, which both are issued by the Flemish government. In addition, there is the local fire department and local communities that will give input to the approval process.
In order to keep the project on schedule, it is important to initiate the work on permits early in the process, and to use consultants with a good reputation and who know the regulatory systems well.

Personnel risks

The performance of a contractor is never better than the individuals assigned to the project. Before entering main contracts, for example with an engineering partner, it is important to review the CVs and, for the most heavily engaged personnel, conduct interviews and check references. This precaution will reduce the risks of poor performance of a contractor.
However, there is still a risk of unforeseen personnel changes due to illness, sudden resignations and other effects outside the contractor's control. The easiest way to mitigate this risk is to have contractors who have a staff sufficiently large and flexible to accommodate the project quickly with good replacement personnel.

Accidents and incidents

Unwanted incidents during the project is foremost prevented by the safety culture and work procedures of the project owner and the contractors. In addition, there are regulatory provisions that the project organisation and contractors have to comply with. In Belgium, in a project like this one, a dedicated safety coordinator must be assigned to the project.
In the last instance, a solid insurance policy for the project phase must be in place.
All the measures mentioned above will contribute to site safety, and minimise the risks of accidents and incidents during work on site. Owner and EPCM contractor should be very strict and firm on safety regulations agreed at the start of the project. This is required to set a correct trend and safety attitude during the construction phase on site. Correcting a bad safety attitude is important, but awarding a good safety attitude is even better.

Technology risks

Kebony has developed its own proprietary production processes. Therefore, the responsibility for the feasibility of the processes will always lie on Kebony as the technology and project owner. Even in contract scenarios where an engineering firm is willing to deliver a complete plant at a lump-sum basis, the contractor will not take responsibility for the feasibility of the production process. The way to mitigate risks and uncertainties in the process technology is simply to build on learning from pilot scale and previous full-scale process development and production.

Budget and progress risks

Risks of financial and schedule overruns are probably the biggest daily risk concerns in a project. All risk factors mentioned above will also entail financial risks and risks of delays.
There are ways to actively mitigate and minimise such risks:

- A good, stable financing package for the project. Inadequate funding will itself easily lead to higher costs through sub-optimisation and increased use of contractor time. The golden rule should be that the financing is in place when the green light is given for the EPCM phase.
- Project management. A vigilant project management, both by owner and main contractor, to capture changes and unforeseen developments as early as possible.
- Professional procurement procedures. This is done through the EPCM partner, and their procurement "machinery" is essential.
- Reporting procedures. Frequent financial and progress reports up through the chain from vendors and sub-contractors through EPCM contractor and to owner is of utmost importance for keeping track of developments and give the project management a shared picture and possibilities to intervene with corrective actions.
- Incentives. The EPCM contractors may be motivated commit extra efforts if there are bonuses or penalties connected to project milestones and budgets.

RESULTS

Kebony Clear production capacity

The technical bottleneck in a Kebony production process is the curing and drying step. To ensure that this step could be performed with the capacity foreseen in the design basis, a lot of attention has been paid to the detailed design of the drying kilns where this step is performed.
After initial start-up operations it quickly became clear that the kilns operated as designed, and delivered the required Kebony Clear capacity and quality with a handsome margin. For Kebony this is a real accomplishment, since the drying kiln design has several important special features that are designed by Kebony's own team, with the aim to cure and dry the Kebony rapidly and uniformly, while recycling the aqueous condensate from the drying step.

Product characteristics

Kebony Clear is clear grades of radiata pine sapwood treated by the Kebony process. The process gives the product increased hardness, dimensional stability and decay resistance, making the products suited for outdoor use in Use Class 3.2, especially decking and cladding.
As described by Lande (Lande 2018), the treatment level and consequently the decay resistance of Kebony products are correlated with the equilibrium moisture content (EMC) of the products, and for Kebony Clear it has been established that as long as the EMC not exceeds 6.2 %, the decay resistance will meet Durability Class 1 criteria according to EN 350-1.

Batches produced in Kebony's new plant comply with this criterion with a good margin.

During the first two months of Kebony Clear production in Belgium, the average EMC was 5.25%, and no batch had an EMC above 6.2%.

CONCLUSIONS

Kebony has built a new production plant in the port area of Antwerp Belgium. The project has been successfully completed on budget, and the plant is now producing Kebony Clear products based on clear grades of radiata pine.

The characteristics of the produced Kebony are well inside the established quality frames, and the production rate shows that the capacity requirements of the design basis are met. Kebony's new production plant will thus give Kebony the production capacity to grow further in Europe in the coming years.

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Improved dimensional stability of polypyrrole enriched spruce as an indication for chemical change

Andries van Eckeveld[1], Raby Malki[2], Michael Sailer[3] and Jacco Eversdijk[4]

[1]Innovita advies & projectbegeleiding, De Zaan 40, NL-3448 BS, Woerden [andries@innovita-advies.nl]
[2]Mevo Houtindustrie, Gerstdijk 15, NL-5704 RG, Helmond [r.malki@mevohoutindustrie.nl]
[3]Saxion University of Applied Sciences, M.H. Tromplaan 28, NL-7513 AB, Enschede [m.f.sailer@saxion.nl]
[4]TNO, High Tech Campus 25, NL-5656 AE, Eindhoven [jacco.eversdijk@tno.nl]

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ABSTRACT

Worldwide activities are initiated in order to work on sustainability. The utilization of local timbers as bio-based materials for building purposes like façades contributes to this development. The polymer polypyrrole could contribute to the utilization of such timbers like spruce. Earlier investigations have shown the potential of polypyrrole in combination with wood and textiles. The aim of this paper is to assess indications of change of the wood structure after *in situ* polymerization of pyrrole in spruce with ferric chloride as an oxidizing agent. The divergent shrinkage and swelling properties of polypyrrole enriched spruce and untreated spruce measured in this research indicate changes in the wood structure. The effect of both ferric chloride and polypyrrole on the dimensional stability contribute to this indication.

INTRODUCTION

The UN sustainable development goals (SDG) with its specific target areas reflect the worldwide efforts concerning sustainability. The utilization of timbers in façades contributes to several SDG and it seems likely that utilization of timbers for building purposes will increase. The demand for (tropical) wood is increasing worldwide, changing the balance of demand and supply. Countries like China import huge volumes from the whole world. For all these reasons, utilization of local wood species for outside building applications is preferred in Europe. However, timbers like spruce do not always meet the requirements for façades. The service life of both the cladding elements and the finishing are frequently point of discussion. The more natural the finishing, the more desirable it is from the point of view of architecture and of sustainability. The demand for smart building materials (integrating several/more functions) is also a result of this sustainability-development (Oostra and Sailer 2016). Therefore, additional treatment(s) of local timbers could improve timber availability for outside building purposes in the coming decades.

In the past decades, a number of new treatments have been developed and introduced to the market. Well-known examples are thermally and chemically modified woods (Homan and Jorissen 2004; Rapp 2001). Other treatment principles are based on water repellence or combinations with wood modifications (Homan and Jorissen 2004; Hyvönen 2005; van Eckeveld 2001). Recently, a timber (surface) treatment with a biofilm has been developed (Sailer *et al.* 2010).

In this context, a combination of wood and polypyrrole (PPy) could be an additional development. In the past, the polymer PPy has been frequently investigated, mainly due to its electrical conductivity (Das and Prusty 2012; Wang *et al.* 2001). The possibility of bio-synthesis of pyrrole (Py) from waste or rest material from agricultural production would meet sustainability requests (Sailer *et al.* 2015). During a 'RAAK-mkb' project at Saxion University of Applied Sciences (Enschede NL) in the period 2015-2017 the technical potential of PPy in combination with wood and textiles for the building sector was explored. The main focus was put on the utilization of spruce (Van Eckeveld 2018). Enriching spruce and textiles with PPy changes the appearance of the treated surface into an unique black to anthracite colour. PPy has a conjugated polymer backbone, which is able to absorb all light, resulting in the dark but (semi-) transparent colour. The wood structure remains visible, giving the final product a typical appearance.

There are several ways to enrich spruce with PPy, but in general *in situ* polymerization is preferred to get penetration of PPy in the wood surface. Principally, several oxidizers could be used, but in this study the focus is put on the use of ferric chloride (iron(III)chloride or $FeCl_3$). The enrichment of spruce with PPy was patented by TNO (EP2114643 (B1)) and further developed in a 'Small Business Innovation Research' (SBIR) project to a production on pilot scale (2012-2014). This first concept (PPy 1.0) was improved during a RAAK-mkb project at Saxion University, resulting in a second (PPy 2.0), in which linseed oil was added.
From laboratory tests and pilot projects it was learned that PPy enriched spruce performs quite well. For example, after four years of exposition, the cladding boards demonstrate satisfying dimensional stability (figure 1), despite the higher wood temperature (absorption of NIR and IR radiation by the dark surface) and the resulting tension. This observation raised the question whether PPy treatment changes the wood structure. The main aim of this paper is to assess dimensional stability of PPy enriched spruce as an indication of chemical change of the wood structure. Reduced shrinkage and swelling might indicate such change of wood structure (e.g. Rapp 2001).

Figure 1: PPy 1.0 façade showing dimensional stability after four years of exposition on the south-west face of a detached house in Elden, NL (Picture: Innovita).

EXPERIMENTAL

Sample preparation

Since most of the research on wood was done with spruce, this wood species was used. Samples were collected from a batch produced by Mevo Houtindustrie that was prepared for other tests. The sample dimensions were 5x10x25mm^3 (tangential x radial x longitudinal). Only pure quarter sawn samples were used, eight samples per parameter.

Treatments

Before treatment all the samples were conditioned at 65% RH (relative humidity) and 23°C to equilibrium moisture content (EMC) and weight was determined. After treatment according to Table 1, the samples were conditioned at the same climate conditions in order to calculate the WPG. After reaching the EMC, weight was determined again.

Table 1: Treatment parameters

Parameter	**Treatment**
Reference	No treatment.
Pyrrole	30 minutes submersion in a 5%- solution (v/v) of Py in water.
$FeCl_3$	15 minutes submersion in a 5%-solution (v/v) of $FeCl_3$ in water.
$FeCl_3$ 103	15 minutes submersion in a 5%-solution (v/v) of $FeCl_3$ in water; after 15 minutes air drying, the samples were oven dried at 103°C for 24 hours.
Linseed oil	1 minute submersion in pure linseed oil; after 1 minute the overflowing oil was removed.
PPy 1.0	10 minutes submersion in 2.5%-solution (v/v) of Py in water; 10 minutes drying; 10 minutes submersion in a 2.5%-solution (v/v) of $FeCl_3$ in water.
PPy 2.0	2.5 minutes submersion in a 2.5%-solution (v/v) of $FeCl_3$ in water; after 30 minutes drying, the samples were submersed in a Py/Linseed oil solution of 50% for one minute, after which the overflowing oil was removed.

Testing procedure

Initially, all samples were leached in three cycles. Each cycle consisted of 15 minutes submersion in water at room temperature, followed by 45 minutes drying at 35°C. After leeching, all samples were conditioned at 65% RH and 23°C. Next, all samples were subjected to the subsequent stages of Table 2. The dimensions were measured by using an electronic micrometer and the mass by using a balance.

Table 2: The description of the different stages before measuring size and mass

Moisture conditions	**Remarks**
Saturation	One week after treatment and conditioning, all samples were saturated with water (apart from other parameters). After 30 minutes vacuum (about 150 mbar), the samples were for about 2 hours submersed in water.
65% RH / 23°C	After saturation, the samples were conditioned for one month (34 days).
35% RH / 23°C	The samples were conditioned for 21 days.
Oven drying	After 24 hours, the weight of some samples (parameters) were not stable, therefore 48 hours oven drying was applied to all samples.

Equations

The WPG (weight percentage gain) was calculated according to Eqn. 1. To avoid possible effects of oven drying at 103°C before testing, the WPG_{65} was used (conditioned mass at 65% RH and 23°C). M_{after} represents the conditioned weight (g) after treatment and M_{before} the conditioned weight (g) just before treatment.

$$WPG_{65} = ((M_{after} - M_{before})/M_{before}) *100\% \qquad (1)$$

Swelling (S_{swe}) and shrinkage (S_{shr}) are calculated on the basis of oven dry and saturated dimensions according to Eqn. 2 and 3. $S_{current}$ is the size (mm), after stabilizing at a specific climate and $S_{saturated}$ the maximum size (mm) after saturation. $S_{ovendry}$ is the minimum size after oven drying. Both radial and tangential orientation is distinguished.

$$S_{swe} = ((S_{current} - So_{vendry})/S_{ovendry}) *100\% \quad (2)$$

$$S_{shr} = ((S_{saturated} - S_{current})/S_{saturated}) *100\% \quad (3)$$

The Equilibrium Moisture Content (EMC) is calculated according to Eqn. 4, where $M_{conditioned}$ is the mass (g) after conditioning at a given climate and $M_{ovendry}$ is the mass (g) after oven drying.

$$EMC = ((M_{conditioned} - M_{oven\ dry})/M_{oven\ dry})*100\% \quad (4)$$

RESULTS AND DISCUSSION

Iron effects in wood

Iron ions in organic materials are responsible for several processes. Emery and Schroeder (1974) investigated the effects of iron on wood in acidic conditions. Fenton related reactions could cause depolymerization and oxidation of wood components (Arantes and Milagers 2006). Kolar *et al* (2003) assessed the acid hydrolysis and oxidation, catalysed by ferrous ions, degrading old manuscripts (ink corrosion). Iron ions react with peroxides, resulting from the oxidation of organic material, releasing very reactive hydroxyl radicals. They also refer to the Fenton reaction as mechanism for degradation (Fenton 1894). Fengel and Wegener (1989) also describe oxidation of wood in combination with hydrolysis in the context of paper and pulp industry. The addition of temperature would plausibly increase oxidation by ferric chloride, which was observed at the $FeCl_3$ 103 samples: after oven drying the samples became dark coloured, with a charcoal-like texture. It is very complex to comprehend the effects of iron in wood. However, the assumption that oxidation of wood occurs seems plausible and accordingly the data of this study will be interpreted.

Weight Percentage Gain (WPG)

The linseed oil and PPy 2.0 samples have the highest WPG, which mainly seems caused by the uptake of linseed oil (see Figure 2). The odd difference between the $FeCl_3$ 103 samples and the $FeCl_3$ samples could be explained by assuming oxidation of wood components by $FeCl_3$. By adding temperature, the $FeCl_3$ 103 samples might be further oxidized after 24 hours oven drying, leading to mass loss of roughly 4,3% (see Figure 2: 4,0% minus -0,3%).

After oven drying, the $FeCl_3$ samples would presumably have reached the same order of magnitude of mass loss as the $FeCl_3$ 103 samples in advance. It may be assumed that also during testing oxidation of wood took place. This assumption of ongoing oxidation could explain data in the Tables 3-5.

We could expect that an oxidation process also took place at the PPy samples, which contained ferric chloride. The effect at the PPy samples might be less pronounced, because the amount of ferric chloride was lower (PPy samples were not submersed for 15 minutes in a 5%- solution as both $FeCl_3$ and $FeCl_3$ 103 samples). In addition, the polymerization of pyrrole might have reduced the oxidation of the wood.

The WPG of PPy 1.0 could likely be attributed to the submersion in the $FeCl_3$-solution. The same submersion is applied to the PPy 2.0 samples. Therefore, it seems logical that the WPG of PPy 2.0 minus the WPG of PPy 1.0 is roughly 50% of the WPG of linseed oil samples.

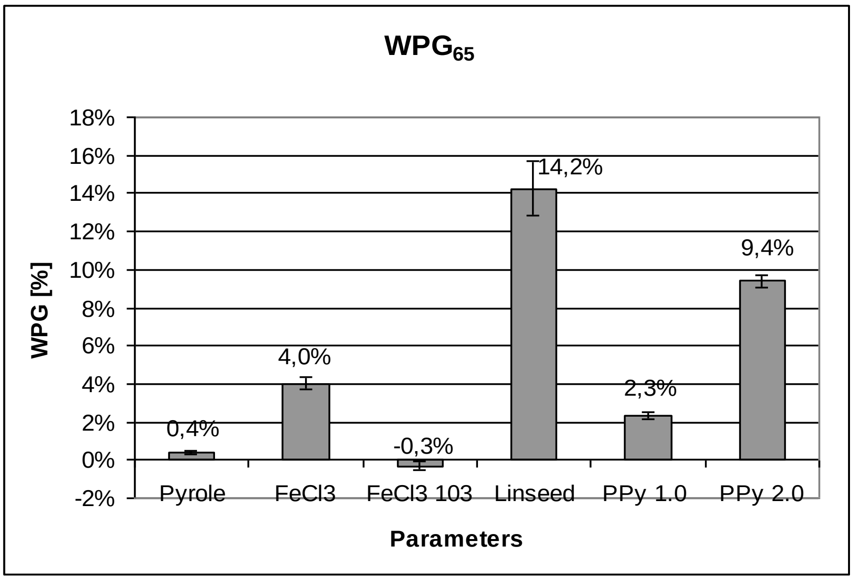

Figure 2: WPG_{65} and standard deviation per parameter

Moisture content

The EMC values at different RH are presented in Table 3. The water repellent capacity of linseed oil could be seen in the reduced liquid water uptake after saturation. Linseed oil is reported to have water repellent properties, even after seven wetting cycles of 96 hours, as is demonstrated for pine (Van Eckeveld 2001).

Table 3: EMC in % at the different moisture conditions (n=8)

RH%	Reference	Pyrrole	$FeCl_3$	$FeCl_3$ 103	PPy 1.0	Linseed	PPy 2.0
saturated	156%	156%	151%	156%	149%	104%	122%
65% RH	12.9%	12.2%	7.3%	16.5%	12.0%	11.3%	12.3%
35% RH	7.8%	7.3%	4.2%	11.3%	6.9%	6.8%	7.4%
0% RH	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%

Although an oxidizing effect of ferric chloride on the wood structure could not directly be determined by calculating the moisture content after saturation, the other moisture conditions in Table 3 indicate this effect. When it is assumed that oxidation took place in the $FeCl_3$ samples during testing, we may expect that mass loss, resulting from the oxidation, occurs. The order of magnitude of mass loss (about 4.3%) fits quite well with the lower EMC for $FeCl_3$ in Table 3. One may oppose that the figures for $FeCl_3$ 103 seem quite odd. However, the assumed influence of temperature, leading to an increased oxidation of wood at $FeCl_3$ 103 samples, could also create additional capillaries in the wood. Therefore, during drying the water evaporation might be slowed down and shrinkage and swelling properties might be affected. The effect of ferric chloride on the other $FeCl_3$ containing samples is more veiled in the average values and will not be discussed further.

Shrinkage and Swelling

The values for shrinkage and swelling of the untreated references are a bit higher than found in literature (Rijsdijk and Laming 1994).

The difference between linseed oil treated samples and the other samples for the EMC after saturation (Table 3), was not reflected by shrinkage and swelling measurements after saturation (Tables 4 and 5). The shrinkage and swelling of the $FeCl_3$ 103 samples equals the linseed oil treated and PPy 2.0 samples at saturation. This could be seen as an indication for the combined effect of ferric chloride and temperature (103°C) on the wood structure, resulting in reduced shrinkage and swelling.

Table 4: Tangential and radial shrinkage (n=8)

Average tangential shrinkage [%]							
RH%	Reference	Pyrrole	$FeCl_3$	$FeCl_3$ 103	PPy 1.0	Linseed	PPy 2.0
saturated	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%
65% RH	5.7%	5.3%	6.3%	3.6%	5.1%	4.9%	3.7%
35% RH	7.9%	7.3%	8.1%	5.7%	7.2%	6.8%	6.1%
0% RH	10.4%	9.7%	9.7%	9.0%	9.6%	9.0%	8.5%
Average radial shrinkage [%]							
RH%	Reference	Pyrrole	$FeCl_3$	$FeCl_3$ 103	PPy 1.0	Linseed	PPy 2.0
saturated	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%
65% RH	2.5%	2.3%	2.9%	1.8%	2.3%	1.9%	1.9%
35% RH	3.7%	3.4%	3.9%	2.9%	3.8%	2.9%	2.8%
0% RH	5.3%	5.0%	5.0%	4.3%	5.0%	4.3%	4.3%

The relation between the values of $FeCl_3$ and $FeCl_3$ 103 samples for swelling seems to be rather contrasting in relation to the shrinkage values. It should be taken into consideration that all swelling values are calculated, using measurements after oven drying (Eqn. 2). Shrinkage however is calculated by using measurements at saturation (Eqn. 3): thus, the oven dry dimensions are only used for calculating the total shrinkage. The oxidizing effect of ferric chloride during testing appears to be visible at the $FeCl_3$ samples conditioned at 65% and 35% RH: all swelling data were the lowest compared to other parameters, but the highest of the shrinkage data.

Table 5: Tangential and radial swelling (n=8)

Average tangential swelling [%]							
RH%	Reference	Pyrrole	$FeCl_3$	$FeCl_3$ 103	PPy 1.0	Linseed	PPy 2.0
saturated	11.6%	10.7%	10.7%	9.9%	10.6%	9.9%	9.3%
65% RH	5.2%	4.8%	3.7%	6.0%	5.0%	4.5%	5.2%
35% RH	2.8%	2.7%	1.8%	3.7%	2.7%	2.3%	2.7%
0% RH	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%

Table 5: Tangential and radial swelling (n=8) (continued)

Average radial swelling [%]							
RH%	Reference	Pyrrole	$FeCl_3$	$FeCl_3$ 103	PPy 1.0	Linseed	PPy 2.0
saturated	5.7%	5.3%	5.2%	4.5%	5.3%	4.5%	4.5%
65% RH	3.0%	2.9%	2.2%	2.7%	2.8%	2.5%	2.5%
35% RH	1.8%	1.6%	1.1%	1.6%	1.3%	1.5%	1.6%
0% RH	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%

The shrinkage of the $FeCl_3$ samples at saturation is slightly lower compared to the untreated reference at saturation. But during five weeks conditioning at 65% RH and 23°C, ongoing oxidation of wood might have resulted in mass loss and extra shrinkage (see the values at 65% and 35% RH in table 4). The low swelling of the $FeCl_3$ samples may reflect the dimensional change including the oxidizing effect, because the oven dry dimension is used for the calculation.

The accelerated oxidation of the $FeCl_3$ 103 samples might likely have resulted in mass loss (as seen in the WPG) and is achieved before saturation. Resulting capillary effects might slow down the evaporation of water after saturation, resulting in a higher EMC and a lower shrinkage at 65% and 35% RH. The high swelling data (Table 5) may reflect the slower evaporation due to capillary effects, which is also visible in the rather high EMC at different RH (Table 3).

PPy effect

The oxidizing effect of ferric chloride might also be visible at the PPy enriched samples (problably not as strong as at the $FeCl_3$ samples). This might be reflected in the rather high shrinkage values of PPy 1.0 compared to PPy 2.0 and linseed oil treatment (but not as high as the shrinkage values of $FeCl_3$ samples). The rather low amount of PPy in PPy 1.0 samples might have limited the possible effects of PPy.

The effect of PPy on the shrinkage might be seen in Table 4 at the PPy 2.0 samples. The total amount of PPy in the PPy 2.0 samples is substantially higher compared to PPy 1.0. The assumed ferric chloride oxidation would be the same as of the PPy 1.0 samples (same submersion conditions). The effect of linseed oil on shrinkage and swelling would be half the amount in the case of PPy 2.0 samples (the linseed oil uptake amounts 50% of the linseed oil treatment). Given these considerations, the rather low shrinkage observed for PPy 2.0 (compared to the shrinkage of PPy 1.0 and linseed oil treatment) could be attributed to PPy itself. The PPy effect on swelling is presumably hidden behind the effect of ongoing oxidation resulting in mass loss and extra shrinkage.

CONCLUSIONS

Does improved dimensional stability of PPy enriched spruce indicate chemical change of wood structure? Iron is reported to be capable of wood depolymerization and oxidation, although the mechanism is complex. The variant behaviour of $FeCl_3$ treated samples during wetting and evaporation indicates change of the wood structure, likely caused by oxidizing effects of ferric chloride. The low shrinkage in this assessment observed at PPy 2.0 samples seems to reflect the share of PPy, together with linseed oil and ferric chloride.

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Practical experience of acetylated wood fibre panel products in Dutch door manufacturing

Jeroen Lückers[1, 2]

[1]Wood2know, Daalseweg 338, NL-6523 CE, Nijmegen [e-mail: info@wood2know.nl]

[2] Kegro Deuren BV, Industrieweg 25, NL-6562 AB, Groesbeek

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INTRODUCTION

Acetylated pine fibre MDF (A-MDF) panels are currently frequently used in exterior doors in the Netherlands, where traditional wood fiber panels have technical difficulties and are, in public opinion, regarded as unsuited since long. The building methods and climate conditions in the Netherlands, combined with market demand of mainly opaque lacquer finishes, gave the acetylated MDF panel a very quick and successful market entry.

In the Netherlands, experience is gathered mainly in exterior, flush panel doors, traditionally made with thin WBP plywood or special HDF types as facing. This subjective review presentation states practical experience in the use of A-MDF in doors, and compares A-MDF physical and mechanical properties in its effect on door behavior, compared to traditionally used waterproof thin HDF and thin WBP plywood. The practical experiences and test results will be shared in a property specific approach.

PRATICAL EXPERIENCES

Exterior doors background

Exterior doors, being a non-stationary part, are among the most demanding parts of joinery in the exterior façade. The Dutch building style, where the door face is typically fully weather exposed situated, additionally has a demanding influence on its performances, mainly those not in the EN 14351-1 included, like maintenance interval and ability to remain fully functional throughout the seasons. Combined with a market that is typically divers, that does not allow for standard stock models and sizes, but demand custom made products makes it a challenge for door leaf manufacturers to produce products that withstand the risks and will not deplete the wood image.
Roughly one can distinguish two basic wooden door types. Either the door is basically a flush panel of wood based panel products, or a solid timber joinery type frame with glass and wood based panel infills.

<u>Wood based panel products for door skins, structural facing, in flush door panels.</u>
A typical construction of a flush panel door consists of a wooden framework, a core material and a structural facing. Thin WBP-plywood or exterior quality MDF/HDF is commonly used. HDF and MDF are used for their workability and finishing quality, combined with a lower price and better availability than thin, exterior glued plywood. The risk of swelling is however restricting its use to only several producers that developed an adequate lacquering system.

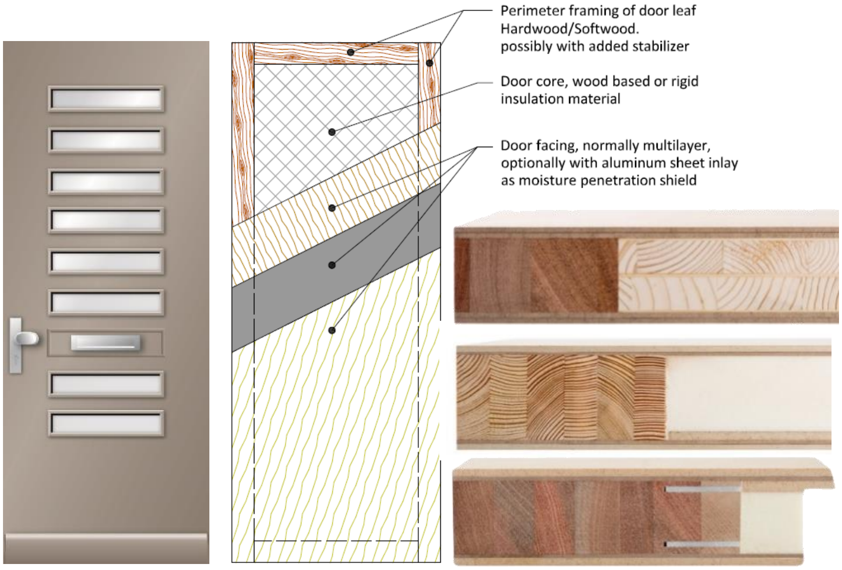

Figure 1: typical constructions for wooden flush panel doors

An exterior wooden or wood based door is to be classified in use class 3.2 according to EN 335. External, not in contact with the ground, however the inner face of the door is situated in use class 1 or 2 (internal situated, occasional humid, but generally dry conditions). The resulting equilibrium moisture content is generally differing between the inner and outer face, influencing the dimensional stability (bending tendency) of the door leaf. To minimize this hygroscopic influence it is not uncommon that a thin aluminum layer is glued into the facing. This mainly prevents the transport of humidity into the underlying construction. Where only the outer layer of facing is still susceptible to moisture content induced shrinking and swelling, the amount of wood material actively taking part in deforming the door leaf is reduced, while at the same time improving the tensile strength in the panel, creating a stiffer door.

Although there is a significant market for UV-stable HPL skins and high end veneer with translucent lacquer finishes, the vast majority of wood based flush panel doors are opaque film finished. The aesthetic performance (except the ability to apply a smooth coating finish) of the wood panel product is therefore inferior to the physical properties, especially strength and hygroscopic dimensional stability. Acetylated wood fiber panel product, having a lower shrinking and swelling coefficient, and still a rather smooth and homogenous appearance, is mainly therefore successfully introduced in the Dutch door industry.

Figure 2: typical constructions for wooden joinery type doors, with possible (moulded)panel infill

Wood based panels as panel infill in joinery type solid timber doors

Typically a more traditional door leaf construction, a joinery construction of wooden stiles and rays, with wooden or glass infill panels (figure2). In this construction A-MDF can be used as infill panel for opaque finished doors with possibility for additional mouldings. Generally competing with WPB Plywood or Exterior grade HDF. Experiences with A-MDF in this field of usage are mentioned especially in machinability and the mechanical property section.

Stability, in between two different climates

Dutch building regulations prescribe a door opening height of at least 2.3m since 2003. Together with an increasing demand in air tightness of the door set due to energy efficient building, the stability of a door panel in bow, warp and twist has become increasingly important. This behavior between 2 climates is determined in accordance to EN 1121. Climate C is for Dutch market regarded as sufficient. The difference in climate (Climate C: 23°C and 30% RH versus 3°C and 85% RH) results in a deformation of the leaf, which is measured according EN 952 and classified according EN 12219 into 3 classes indicating the stability of the product for the end consumer.

Door test experiences and results

Comparing 3 commonly used thin exterior quality HDF (all .5 - 3mm) with A-MDF currently available on the market, show a factor 4 better stability in length and width direction (See table 1). To test if this better dimensional stability of the panel has effect on the total doorleaf doors should show less deformation in an EN 1121 test.

Table 1, overview of properties of regular exterior HDF 3mm versus A-MDF 4mm, source: product datasheets of the producers, combined with actual quality inspection experience (values in brackets)

Property		**Unit**	**Test method**	**Exterior MDF producer 1**	**Exterior MDF producer 2**	**Exterior MDF producer 3**	**A-MDF 4mm**
Density	min	kg/m³	EN 323	840	880	820	760
Internal bond	min-max	N/mm²	EN 319	1.5 (1.8 - 2.2)	1.9 (2.0 - 2.4)	1.2 (1.2 – 1.8)	0.9 (0.7 – 1.1)
Moisture content on delivery	max	%	EN 322	(5,5 - 7.5)	(7 ±3)	(5 – 8)	(2 – 4)
Thickness swelling after 24h in water	min	%	EN 317	18 (15 - 20)	18 (14 – 18)	12 (8 – 12)	2.3 (1.5 – 2.5)
Internal bond after 2h in boiling water	min	N/mm²	EN 1087 / EN 319	(0.8 – 1.2)	0.8 (0.8 -1.2)	0.7 (0.9- 1.2)	0.65 (0.6 – 1.1)
MOR	min	N/mm²	EN 310	48	60	40	28
MOE	min	N/mm²	EN 310	4800	4000	3500	3000
Stability in thickness	max	%	EN 318	5.0	6.0	n.a.	1.0
Stability in length	max	%	EN 318	0.4	0.4	0.3	0.1
Surface absorption	min	mm	EN 283-1	150	150	n.a.	150
Formaldehyde	max	mg/100g	EN 120	1	1.5	1.0	1.0
Thermal conductivity EN 13986 *		W/m.K	EN 13986	0.159	0.172	0.153	0.136

** thermal conductivity determined via interpolation table 11, EN 13986:2004*

A practical screening in 2012, illustrated in figure 3 shows the dimensional stability of 4 door types with different facings. A-MDF compared to HDF facings from producer 1 and 3 (table 1). Door 1 to 3 had similar construction and identical leaf size, all with an aluminum sheet incorporated in the facing.

This screening showed no obvious difference between 3mm exterior HDF top facing (door 1 and 3) and 4mm A-MDF(door 2) however if used only A-MDF 6mm (door 4) without aluminum sheet in the facing, the resulting door is considered less stable.

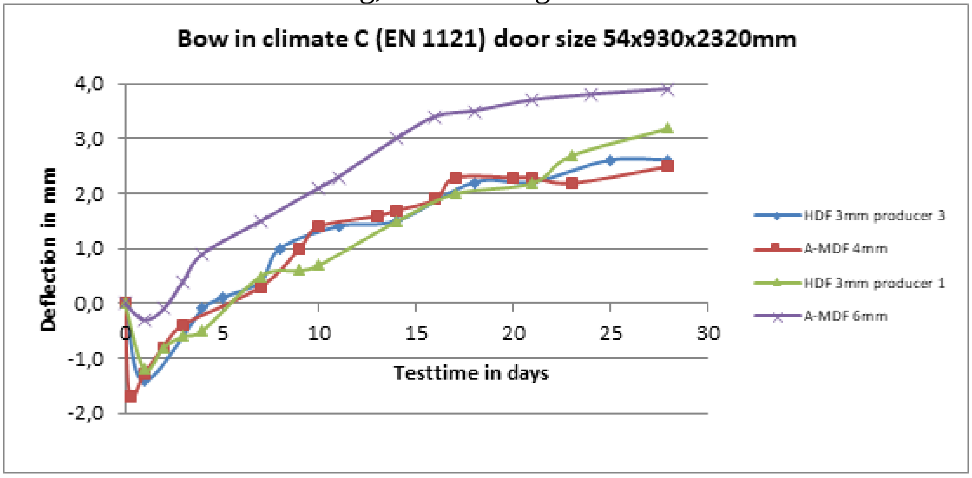

Figure 3: dimensional stability of 54mm door with 4 different door facings, all incl alu inlay, except A-MDF 6mm.

Stability of the end product has not improved despite the use of a more dimensional stable acetylated MDF, possibly caused by the additional thickness of the outer facing. While total door thickness remains 54mm, the position of the aluminum sheet is positioned more in the direction of the core, reducing frame and core thickness, thus slightly reducing core stability, and increasing the amount of material subjected to hydroscopic and thermal changes. Above statement is based on a single measurement sample As the tests are relatively expensive and time consuming, and while EN 13251-1 (CE) and AD0803 (national) regulations also only prescribe 1 successful test to declare a certain stability class , they are often indicatively determined and only 1 door per variation is tested.. As the stiffness of the wooden framework, with normal wood variation, is of important influence on the stiffness of the door leaf, it would be interesting to relate a measured stability of the end product to a measured MOE of the door style on the lock side. Secondly of interest would be to find a relation between moisture content induced shrinking and swelling, and the resulting force the panel develops.

Dimensional stability of interior doors

Where dimensional stability due to different climates is obvious in exterior doors, interior functioning doors normally also separate 2 different climates. A straight door gives advantages in sound insulation values, smoke tightness and fire resistance performances. Adding an aluminum sheet in the door facing is therefore also relevant for interior doors in some cases. The improvement of shrinkage/swelling coefficient of acetylated MDF could make the added aluminum inner facing layer obsolete. By adding a sufficient stable frame, several producers already practically proven to be able to produce sufficiently stable doors, without the aluminum layer. Figure 4 shows

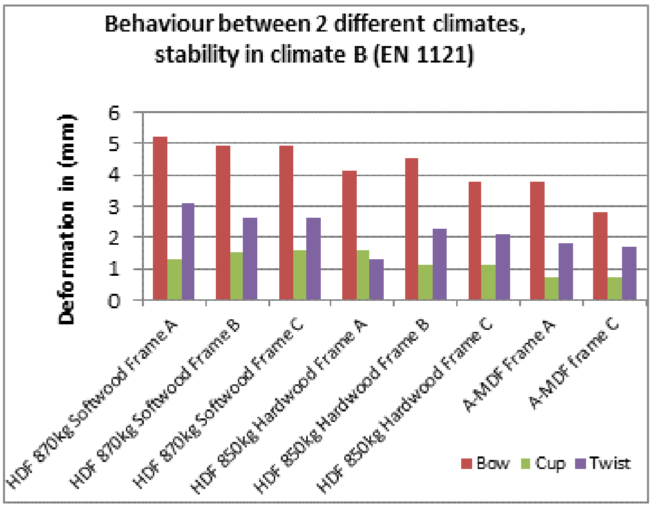

Figure 4: dimensional stability of a 40mm interior doors with 2 different types of HDF facing versus A-MDF. n=1

a screening test result of interior doors in EN 1121 test climate B. The results by a Dutch interior door manufacturer in German laboratory, show a trend of improvement with improved stability of the fibre panel facing.

Effect on door leaf size Although there is a 4 times better stability in A-MDF compared to regular interior quality HDF, 0,1% of 2,3m door height is still 2.3mm. In terms of doors this a lot, considering the gap of plain edged wooden doors are commonly only several mm, this could lead to jamming doors. An aluminum inlayer in the facing has practically proven not to have such issues. Doors with aluminum facing will stay at production size +/- 0.5mm throughout their service life

Machinability, experience in routing and mouldings

Machinability is a rather subjective topic and experiences may differ between producers. There can be some advices drawn from experience over the past few years. Where acetylation reduces the EMC of the fibers and resulting MDF panel hardly shrinks and swells, the mechanical properties are not at the level of regular thin HDF (see table 1). These express during tooling. It generally works easy, however to generate clean panel edges and mouldings, the tools have to be sharp and more in a softwood configuration. Compared to regularly used exterior grade HDF, A-MDF is coarser and less dense. The resin content in traditional HDF is considered to also results in higher wear on tooling. However due to its high density the edge generally stays smooth even with slightly blunted tools. To prevent wear, diamond plated steel knifes are generally used in the radius cutter on the panel edge. Diamond being less sharp, results in an edge quality in A-MDF , as shown in figure 5, that can be uneven.

A-MDF faced door leaves are more susceptible to scratches due to a lower surface hardness, this is mainly important in the production environment of heavy door leaves, where handling these previously was not a risk, internal transport and handling require additional attention.

Sanding is easier, although the surface of acetylated MDF is rougher than regular HDF and MDF, the surface is easily smoothened by applying with fine sandpaper grid >220. A slight touch is enough. Probably a positive side effect caused by the brittleness of the fibre, influenced by the acetylation process and the low EMC.

Thin okoumé plywood, also traditionally used in exterior Dutch doors, is normally know to have problems with edge profiling and moldings. Wood fiber texture, and thickness of the cross layers in the plywood, determines the machinability. Compared okoumé plywood, A-MDF is easier machined, with a higher finish quality, especially for decorative mouldings

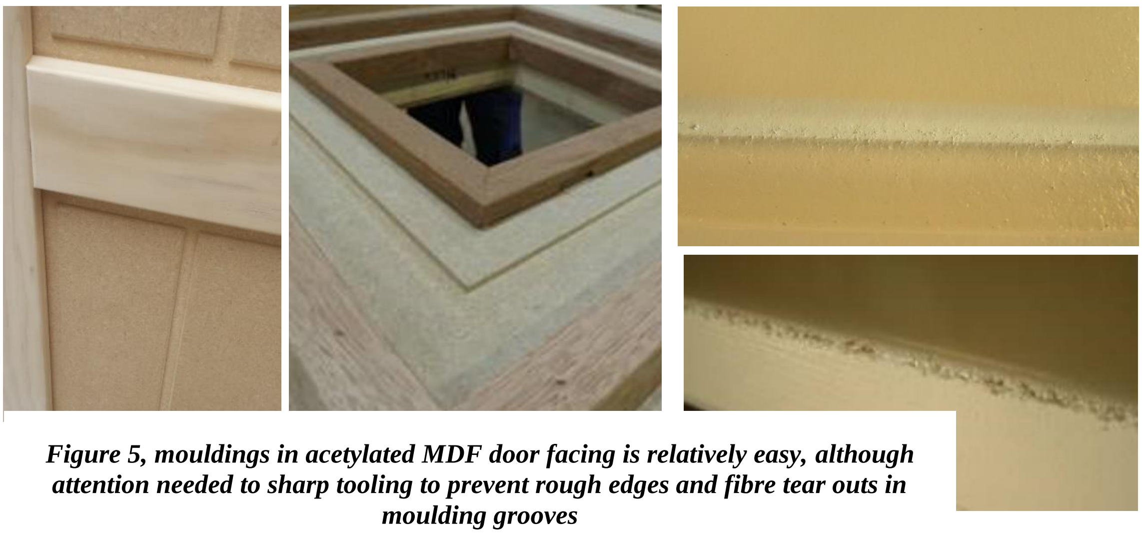

Figure 5, mouldings in acetylated MDF door facing is relatively easy, although attention needed to sharp tooling to prevent rough edges and fibre tear outs in moulding grooves

Dutch VOC regulation lead to general ban of industrial use of traditional solvent based paints starting from 2003. Waterborne alkyd and acrylic paint systems have since then been the standard.

Comparing to plywood, the surface of acetylated MDF is smooth and free of grain rise, which, especially with water dispersed paint systems, is a common problem.

One should be aware though that the surface of acetylated pine fibre MDF is less dense than normal MDF or HDF. This results in a very fibrous finish after the first basecoat layer on acetylated MDF. Part of the 1st paint layer will also penetrate the surface, thus reducing the dry film layer thickness of this layer. Although the resulting film layer is less thick, there is no negative effect from the field experience known until now. Several paint suppliers even increase their guaranteed maintenance intervals if the paint system is applied on A-MDF.

The introduction of water based paint systems introduced an increase in swelling of the exterior HDF compared to the use in combination with solvent based paint systems. The substance used to dissolve the acrylic in water interferes with the hydrophobicity of the HDF surface. A finished exterior HDF panel, with a damaged paint layer, will visually show more swelling when exposed to water immersion than the same panel without paint finish. Also the swelling below the paint expands over a large surface. The water is capillary transported in the surface of the HDF in the contact area with the paint film. The paint film prevents quick evaporation, and thus causing swelling of the fiber, which shows as visual disturbance in the paint film. Compared to the matte surface of HDF, the glossy paint surface will highlight the experienced swelling.

Although in the past 15 years the paint systems have radically improved and with the right care, the issue above is less of a risk. The HDF door skin nowadays has serious image issues due to these technical problems in the past. By changing HDF for A-MDF, the effect of swelling is largely invisible. The water uptake however is still present. The acetylated fibers hardly take up water in the cell wall, making the panel very stable, however it does take up water in the cell lumen and cavities in between the pressed fibers. The capillary effect may even be increased because of closing off the cell walls.

Figure 6: Left: swelling in a traditional exterior HDF door, Swelling trough capillary water from letterbox, also resulting in blistering in the paint. Right, detail of a glass bead on an A-MDF door, due to a failing seam there is water uptake in the panel. It does not show swelling, but blisters indicate paint film adhesion failure, after drying the paint adhesion can recover.

A way to simulate the risk of moisture underneath the coating, is the Paint – Scratch and Bubble test (PSB-test). Developed with SKH/SHR and refined by intense use in the QA lab of Kegro Deuren, it has no official, normative state. A coated sample is scratched by applying a controlled knife cut, and a drill hole of 8mm. The sample is than immersed in water 20°C +/- 3°C for 24h. After which the swelling of the substrate is visually inspected and measured in mm from the applied damage.

A swelling more than several mm from the scratch is revered as insufficient for use in exterior doors. The test result is always an interaction between both wood panel substrate and the paint system. The same panel can show different behavior with different paint systems.

Additionally the effect can be increased by raising water temperature, or by applying the same test sample in an accelerated weathering test used in exterior door standard AD0803, which alternates with waterspray, IR irradiation, and frost (-10°C) for 6 subsequent weeks. Especially the addition of temperature by IR directly after water is sprayed on the damaged surface, will lead to a higher water uptake and therefore also increased swelling of the substrate.

The PSB test is done to simulate mechanical damages that can, and usually will, occur during construction phase and regular use of the door. Secondly water penetration can occur where (capillary) seams develop in added wood mouldings, glass beads, and surface attached building hardware.

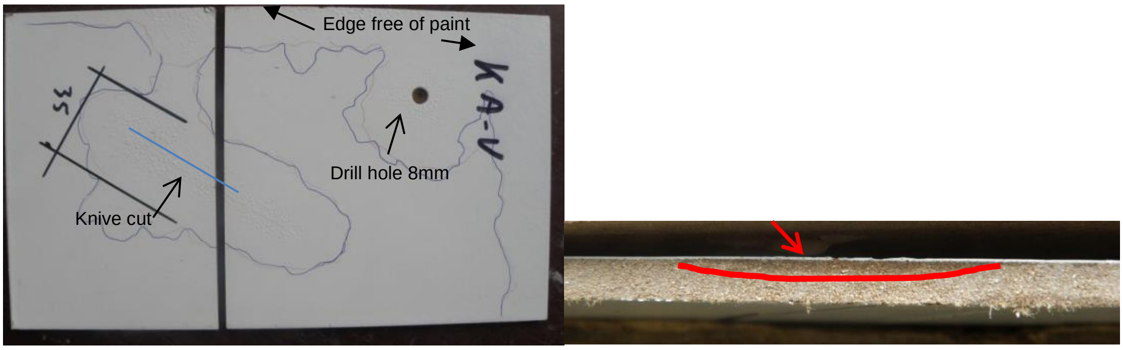

Figure 7: an example of a PSB test in exterior quality HDF, swelling outline is marked on the surface. Crosscut through swelling reveals the spread of water in the fibres marked in red.

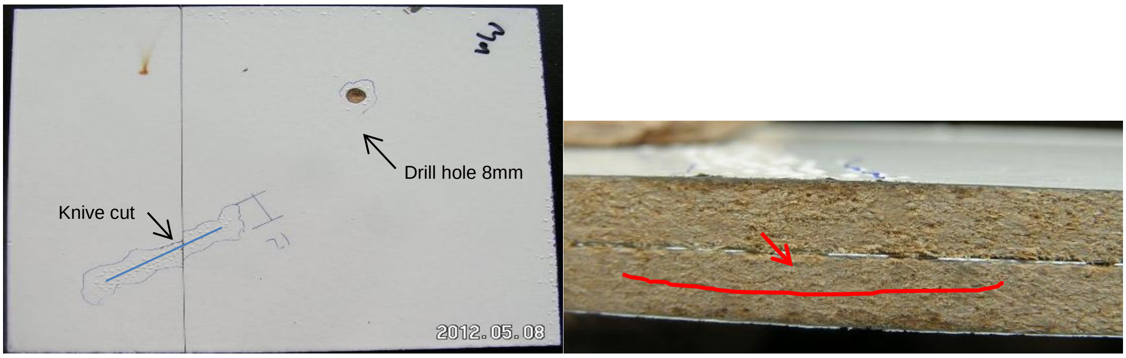

Figure 8: an example of a PSB test in acetylated MDF, although no obvious swelling in the sample, there is paint adhesion failure (marked area). The crosscut revealing water in the panel surface, marked in red

Effect of A-MDF mechanical properties on a door

Important in the prevention of paint film damages is the surface hardness of the door facing. This property is not only based on the panel, but also the underlaying structure, as well as the quality of the paint film.

The quality of surface hardness is classified according EN 1192: 1999, where the impact resistance is determined with a hard object according EN 950: 1999. A steel Ø50mm ball is dropped on the door with an impact strength of 1, 3.5, 5, or 8J , The classification is based on imprint diameter and depth not exceeding 20mm resp. 1mm. Additionally no cracking and flaking of the surface is allowed.

Dutch AD0803 requires class ≤ 3 (5J). Which is easily reached with HDF or Okoumé thin plywood (5-8mm) facing (normally class 4), With A-MDF in 4 and 6mm thick facing, a class 3 is generally reached. Sufficient, but indicating a slightly higher risk of mechanical damages.

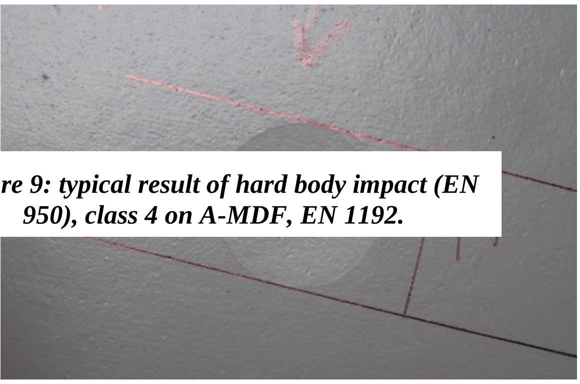

Figure 9: typical result of hard body impact (EN 950), class 4 on A-MDF, EN 1192.

Apart from a risk on the surface of the door, there is also a risk of mechanical damage on the corners, especially the bottom corners (during fitting) and the lock side (damage due to bumping into the door). Also the edges are susceptible to chipping. The lower internal bond, and the tendency to split due to an impact load parallel to the fiber surface are a point of concern in the resulting door quality, increasing the edge radius is a basic solution that reduces the risks.

<u>Burglar resistance</u>

Dutch building regulation demands burglar resistance class 2 (EN 1627:2011) for all "reachable" doors and windows in domestic housing. Meaning all exterior doors are to be fit for high impact resistance. The effect of mechanical properties of the wood panel product used is most evident in glass fitting, where the door facing is adding subsequent screw holding strength, and in moulded door panel fitting. Solid wood joinery type doors, fitted with panels in a rebate. In case the panel is made of A-MDF, it should withstand the standardized dynamic impact forces as applied by EN 1629: 2011. In this test a pendulum 50kg load from a 45cm drop height in both the center of the panel as oriented towards the corners, may not create an opening in the construction

Test by Kegro deuren on moulded panels (figure 10) show additional measures need to be taken with A-MDF to prevent internal failure of the panel upon impact. Where in the case of traditionally used solid timber or exterior MDF panels the fitting technique is decisive, in case of acetylated pine fibre MDF the internal strength can lead to failure even if the fitting is complying.

Figure 10: impression of a typical insulated, panel infill construction, with moulded edge profile. In a dynamic burglary resistance test (EN 1629)

Thermal conductivity, an important value for exterior doors

The thermal conductivity (ʎ) of already in market wood panel products are mostly not specifically tested in an EN 12664 test, but always been validated based on density as stated in table 11, EN 13986:2004. The conductivity is density related to be determined on interpolation from the given values. These values listed below in table 2, result in a correlation $R^2 = 0.996$ ʎ = $0{,}0323e^{0{,}0019\rho}$

ʎ = Thermal conductivity (W/mK)
ρ = Wood fiber board density in kg/m³

The conductivity of A-MDF is determined according to EN 12664. Results listed in table 3 show an indicative single test value and the equivalent of this value if evaluated according EN 13986:2004. This shows an average improvement in thermal conductivity just by actual measurement, of 19.8%.

Important is to note the possible effect of wood moisture content. The thermal conductivity according EN 12664 is determined after acclimatizing in 20°C and 65%RH. Exterior use likely results in a higher moisture content thus increasing the thermal conductivity.

Table 2, overview of standard thermal conductivity values in relation to panel density

Density (kg/m³)	Thermal conductivity (W/mK)
250	0.05
400	0.07
600	0.10
800	0.14

Table 3, overview comparing actual measurements to standard values. n=1

Th (mm)	Density (kg/m³)	λ measured (W/mK)	λ according EN 13986 (W/mK)	Improvement by measurement
4	755	0.105	0.136	22,8%
6	781	0,107	0.142	24,6%
9	736	0,106	0.131	19,1%
12	743	0,105	0.133	21,1%
15	684	0,0998	0.118	15,4%
18	684	0,100	0.118	15,3%

In the total thermal conductivity of a door set, determined according to EN-ISO 10077-1:2017, the calculated effect of the actually determined ʎ improvement in A-MDF, is off less importance in this example (table 4). However if only 1,8%. still a welcome free side-effect for the exterior door industry that is constantly searching for improvements in thermal insulation values.

Table 4, shows an example calculation on a sandwich panel construction with a 40mm Rigid Insulation Foam (ʎ=0.032W/m²K) core and 7mm facings of regular wood panel products compared to the acetylated MDF values (measured) and the value as stated in EN 13986. A maximum improvement of 21 mW/m²K, if compared to exterior grade HDF, is to be reached.

The relative improvement will be enlarged if using a thinner sandwich (insulation core) or a sandwich with a solid wood core, but the below calculation is rather distinctive to regular Dutch exterior door panels.

CONCLUSIONS

Use of acetylated pine fibre MDF as door facing for flush or panel infill for joinery type doors, demands attention as it influences the mechanical properties and abilities of the door. Paint producers increase their warranties on this substrate, though to benefit the most of using acetylated pine fibre MDF, the risk of paintfilm failure and possible need to adopt changes in paint system, is to be considered.

The increased durability of the acetylated fibre is not much of interest in doors, but the outstanding dimensional stability and low thickness swelling in wet conditions of acetylated pine fibre MDF panel improves the general dimensional stability and the expected life span and maintenance interval of doors in weathered exposure. Thus making it very successfully used throughout the wooden exterior Dutch door industry, with technical potential in the interior utility door market.

Table 4, calculation effect of facing on thermal transmittance coefficient (U-value)

Plywood Facings, WPB Okoumé

Material:	**Thickness**	**ʎ-value**	**R_m**	**U-Value**
Plywood WBP Okoumé	7 mm	0,150 W/mK	0,047 m^{2}K/W	
PUR Rigid 50kg/m^3	40 mm	0,032 W/mK	1,250 m^{2}K/W	
Plywoood WBP Okoumé	7 mm	0,150 W/mK	0,047 m^{2}K/W	
Average	54 mm	0,040 W/mK	1,343 m^{2}K/W	**0,661 W/m^{2}K**

HDF Facings, EN 13986 ʎ-Value

Material:	**Thickness**	**ʎ-value**	**R_m**	**U-Value**
Exterior HDF 875kg/m^3	7 mm	0,170 W/mK	0,041 m^{2}K/W	
PUR Rigid 50kg/m^3	40 mm	0,032 W/mK	1,250 m^{2}K/W	
Exterior HDF 875kg/m^3	7 mm	0,170 W/mK	0,041 m^{2}K/W	
Average	54 mm	0,041 W/mK	1,332 m^{2}K/W	**0,666 W/m^{2}K**

Acetylated MDF Facings, EN 13986 ʎ-Value

Material:	**Thickness**	**ʎ-value**	**R_m**	**U-Value**
A-MDF at 760kg/m^3	7 mm	0,137 W/mK	0,051 m^{2}K/W	
PUR Rigid 50kg/m^3	40 mm	0,032 W/mK	1,250 m^{2}K/W	
A-MDF at 760kg/m^3	7 mm	0,137 W/mK	0,051 m^{2}K/W	
Average	54 mm	0,040 W/mK	1,352 m^{2}K/W	**0,657 W/m^{2}K**

Acetylated MDF Facings, measured value

Material:	**Thickness**	**ʎ-value**	**R_m**	**U-Value**
A-MDF	7 mm	0,107 W/mK	0,065 m^{2}K/W	
PUR Rigid 50kg/m^3	40 mm	0,032 W/mK	1,250 m^{2}K/W	
A-MDF	7 mm	0,107 W/mK	0,065 m^{2}K/W	
Average	54 mm	0,039 W/mK	1,381 m^{2}K/W	**0,645 W/m^{2}K**

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Wood modification with DMDHEU (1.3-dimethylol-4.5-dihydroxyethyleneurea) – Status quo and latest research activities

Lukas Emmerich[1] and Holger Militz[2]

[1] University of Goettingen, Wood Biology and Wood Products, Faculty of Forest Sciences, Buesgenweg 4, D-37077 Goettingen, Germany [lukas.emmerich@uni-goettingen.de]

[2] University of Goettingen, Wood Biology and Wood Products, Faculty of Forest Sciences, Buesgenweg 4, D-37077 Goettingen, Germany [holger.militz@uni-goettingen.de]

Keywords: chemical wood modification, cross-linking, dimensional stability, durability, hardness, N-methylol, textile resin

ABSTRACT

Wood modification enables to improve certain characteristics of wood without the use of biocides. The mode of action of corresponding technologies is similar and based on chemical changes in the wooden material. Within past decades much research work was carried out on wood modification technologies so that some have been commercialized until today (e.g. ThermoWood®, ACCOYA®, KEBONY®) or already been in the phase of market launch but did not establish so far (e.g. DMDHEU wood modification). The N-methylol compound 1.3-dimethylol-4.5-dihydroxy-ethyleneurea (DMDHEU) is a water-soluble resin which was originally developed for the textile finishing industry and transferred to wood application the first time in the late 1950s, finding an improved dimensional stability of such treated wood. Within the past two decades fundamental and applied research work was carried out on that topic at the University of Goettingen (DE). These investigations proved an enhanced dimensional stability, biological durability, hardness and weathering performance for DMDHEU treated wood and were the basis for upscaling this technology to a pilot scale process for Scots pine (*Pinus sylvestris* L.). The latter was done in the context of a joint project with BASF AG (Ludwigshafen, DE). Although first products (brand name: Belmadur®) reached market maturity in 2010, market penetration was finally not reached due to internal marketing decisions by the BASF. In 2016 a new cooperation project arose between the textile chemicals supplier Archroma Management GmbH (Reinach, CH) and the University of Goettingen (DE). In this context, investigations were resumed to forward the market launch and further improve the performance of DMDHEU modified wood. Different permeable fast-growing wood species are subject to further research including treatments with formaldehyde-reduced and formaldehyde-free cross-linking agents and further additives (e.g. flame retardants). Meanwhile, upscaling of DMDHEU treatment for Radiata pine (*Pinus radiata* D.Don) is running in New Zealand and interest from the wood working industry in Europe (mainly: DE, CH, NL) and Brazil strongly is increasing.

INTRODUCTION

Wood modification in principle provides a biocide-free and non-toxic alternative to wood preservatives and improves certain wood characteristics to enable the use of non-durable timber for outdoor applications (Hill 2006). Established wood modification techniques cause chemical changes in wood, either by the use of various chemical agents (chemical modification) or controlled degradation processes due to the application of heat (thermal modification at 180 – 260 °C). Thermal modification processes (e.g. ThermoWood®, PLATO®) are the most common and established wood modification techniques. Besides, impregnation modification processes with reactive chemical agents such as acetylation with acetic anhydride (ACCOYA®) and furfurylation with furfuryl alcohol (KEBONY®), have been commercialized within the past decades (Hill 2006, Mai 2010). In this context, cyclic N-methylol compounds such as 1.3-dimethylol-4.5-dihydroxyethyleneurea (DMDHEU) have been studied for wood application (Xie *et al.* 2014). DMDHEU is a water-soluble glyoxal resin and the most widely used basis of easy-care finishing products for cellulose-based textiles (Schindler and Hauser 2004). The treatment of wood with dimethylol compounds of ethylene urea (DMEU) has been studied in the late 1950s for the first time by Weaver *et al.* (1960) who found an improved dimensional stability of such treated wood. This effect of dimethylol resins was confirmed e.g. by Nicholas and Williams (1987) for further wood species coming along with an improved biological durability (Militz 1993). Thus, initial lab-scale trials with DMDHEU were followed by intensive fundamental and applied research at the University of Goettingen since the 2000s that were focused on the practical feasibility of DMDHEU modification technology (Krause 2006, Schaffert 2006, Wepner 2006, Bollmus 2011). Previously listed investigations were the basis for upscaling DMDHEU technology to a pilot scale process for Scots pine (*Pinus sylvestris* L.) in the context of a joint project between BASF AG (Ludwigshafen, DE) and the University of Goettingen (DE). After successful transfer to wood processing and with upcoming cooperation with the wood working industry (Fa. MUENCHINGER, Fa. VARIOTEC, Fa. BECKER, Fa. FAHLENKAMP) the Belmadur® Technology (brand name) was close to the market launch and first products reached market maturity in 2010. For instance, Belmadur® Pine was certified for window joinery (VFF 2010). However, market penetration was finally not reached once BASF stopped production operation due to internal marketing decisions. Since the Archroma Management GmbH (Reinach, CH) acquired the global textile chemical business of the BASF in 2014, a joint research project with the University of Goettingen (DE) arose and resumed market launch and investigations to improve wood modification technology using DMDHEU (Emmerich 2016).

The overall aim of this study is to review previous and recent findings with respect to wood modification using DMDHEU and its derivatives. In order to clarify the state of the art, focus of this review is put on chemical reagents, impregnation and curing processes as well as wood species tested so far. Consequently, the review covers the effects of this modification technology on wood characteristics and puts them into a common context. In summary, a characteristic profile of the modified wood is to be worked out, as well as those topics which constitute current research needs.

STATE OF THE ART

Modification process

The treatment process is conducted in a two-stage process. Vacuum-pressure-impregnation (1) of wood with a monomer-impregnation solution is followed by subsequent polymerization of the reagent (curing) at temperatures > 100 °C (2). Full-cell impregnation is required. Hence, modification of solid wood is limited to permeable wood species. Different curing processes from textile application have been tested for wood application, with maximum curing temperatures limited at 130 °C (Schaffert 2006). The most common Pad-Dry-Cure (PDC) process describes a curing under dry-conditions in drying ovens and led to high fixation rates, little hygrothermal discoloration and extremely low formaldehyde emissions of the modified timber. However, dry-curing is exclusively suitable for lab-scale samples, since drying before polymerization effects migration of reagent monomers with water. Subsequently, an uneven distribution of reacted DMDHEU along cross-sections of large-size timber was observed after dry-curing (Krause 2006). The solution for drying and curing of large-scale samples was given by means of a curing in superheated steam atmosphere under atmospheric pressure and at curing temperatures of approximately 120 °C (curing schedule: heating – curing/ drying - cooling - conditioning). Homogeneous distribution of reacted DMDHEU, good fixation (> 90% DMDHEU retention after hot-water extraction at 90 °C) and low formaldehyde emissions were achieved for Scots pine, coming along with good drying qualities. Nitrogen content and fixation of treated wood correlate with property improvements and suit for quality assurance of the modification process (Bollmus 2011).

Chemical agents and catalysts

The monomer-impregnation solution consists of reagent, catalyst and water. Mainly the low-molecular-weight N-methylol compound DMDHEU (Figure 1, left), synthesized from urea, glyoxal and formaldehyde (Schindler and Hauser 2004), was used to modify wood in the past (Militz 1993, Schaffert 2006, Wepner 2006, Dieste Märkl 2009, Bollmus 2011). Property improvements but also formaldehyde emissions of modified wood are positively correlated with the applied DMDHEU concentration whereby formaldehyde emissions might be controlled by the use of certain reagents. Ether-modified DMDHEU derivatives (mDMDHEU, Figure 1, middle), reacted with methanol or diethylene glycol (DEG) as formaldehyde scavengers, revealed reduced formaldehyde emissions but fixation and wood characteristics similar to DMDHEU treatment. DMeDHEU (Figure 1, right), synthesized from N,N-dimethyl urea and glyoxal, allows formaldehyde-free modification but revealed a reduced fixation in wood compared to DMDHEU. Therefore, formaldehyde-free resins were considered to be less suitable for wood modification and not pursued at that time (Krause 2006).

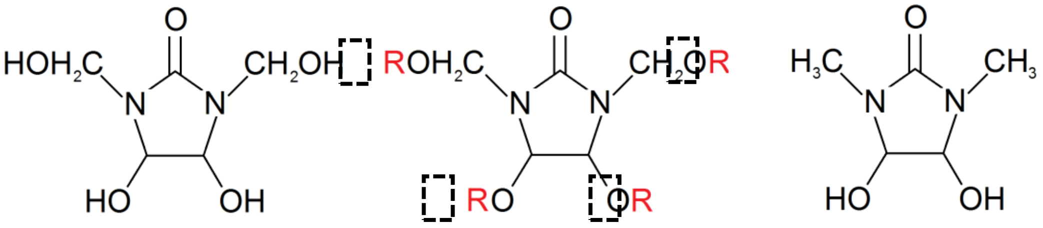

Figure 1: Structural formula of DMDHEU (left), methylolated DMDHEU with R = H or R = CH3 (middle) and DMeDHEU (right, Schindler and Hauser 2004, adapted).

The use of a catalyst led to enhanced reactivity of the reagent and improved material characteristics. So far, magnesium chloride ($MgCl_2$) was found to be the most suitable catalyst regarding high fixation of DMDHEU at benign curing conditions and at the same time good dimensional stability and durability (Krause 2006). Later investigations used magnesium nitrate ($Mg(NO_3)_2$, Dieste Märkl 2009, Brischke *et al.* 2012, Lopes 2013, Emmerich 2016), since it provides similar catalytic effect compared to $MgCl_2$.

Mode of action

Property enhancements via impregnation modification processes occur primarily due to the impregnation of wood cell walls with a reagent that then reacts and causes a permanent *cell wall bulking* (Hill 2006). Positive *bulking* was detected after treatment of wood with DMDHEU, mDMDHEU and DMeDHEU as a key parameter to prove cell wall penetration of the reagents (Krause 2006, Emmerich 2016). Applied at the same concentration level, formaldehyde-free DMeDHEU caused higher *bulking* compared to DMDHEU and mDMDHEU (Krause 2006, Emmerich 2016). Principle reactions of DMDHEU molecules within textiles, such as cross-linking of cellulose molecules and polymerization (autocondensation) via reactive hydroxymethyl groups (Schindler and Hauser 2004), were even presumed for wood. This based on results of Krause (2006) once a 'cross-linking-effect' (reduced maximum swelling at fibre saturation point (*FSP*)) was measured for Scots pine treated with reagents containing reactive N-methylol groups (DMDHEU, mDMDHEU). This ‘cross-linking-effect’ increased with rising DMDHEU concentration. Polycondensation of DMDHEU molecules was found by *in situ* reaction of pure resin and the formation of solid, brittle polymers (Krause 2006). Subsequent trials (Wepner 2006, Bollmus 2011, Emmerich 2016) could not confirm this ‘cross-linking-effect’ and thus not prove mentioned reactions of DMDHEU on molecular level in wood.

Wood species – Solid wood and wood-based composites

Fundamental and applied research on wood modification with DMDHEU was mostly performed with Scots pine sapwood (Krause 2006, Schaffert 2006). Upscaling was attempted with Scots pine and partly European beech (*Fagus sylvatica* L.) wood (Schaffert 2006, Bollmus 2011). Isolated investigations on further permeable wood species e.g. Rubber wood (*Hevea brasiliensis* Müll. Arg., Krause 2006), Slash pine (*Pinus elliottii* Engelm., Militz *et al.* 2011, Militz and Norton 2013) and Radiata pine (*Pinus radiata* D.Don, Derham *et al.* 2017) confirmed a general high-level improvement of biological durability and dimensional stability by DMDHEU modification. Nevertheless, process development and optimization to an industrial scale were limited to Scots pine up to now (Schaffert 2006), since DMDHEU modified beech wood revealed a high amount of drying failures, mainly cracking, even though process optimization was in progress (Schaffert 2006, Bollmus 2011). The applicability and benefits of wood modification with DMDHEU were confirmed also for wood-based composites for instance plywood (Wepner 2006).

Characteristic profile

After fixation of DMDHEU molecules within wood, a new material results in the form of a wood-polymer composite, with the appearance of solid wood. Long-term property changes of wood treated with cross-linking N-methylol compounds were affected by the following parameters (Krause 2006, Schaffert 2006, Bollmus 2011):

- Degree of loading (weight percent gain, *WPG*)
- Curing conditions
- Chemical constitution of the reagent (degree of ‘cross-linking’) and fixation
- Catalyst system
- Wood species

Resistance against biological decay

High resistance against degradation by brown rot (*P. placenta*, *G. trabeum*, *C. puteana)*, white rot (*T. versicolor*) and soft rot fungi were obtained by DMDHEU modification. This was proved in laboratory trials according to appropriate European standards, for solid wood (Krause 2006, Schaffert 2006, Bollmus 2011, Militz and Norton 2013) and also for wood-based composites (Wepner 2006, Dieste Märkl 2009). Fungal activity and degradation decreased with increasing degree of loading (*WPG*) so that durability class (DC) 1 (‘very durable’) can be reached following CEN/TS 15083-1 (2005) what was proved for DMDHEU modified Scots pine and European beech (Verma *et al.* 2009). Field tests above-ground (UC3) and in-ground (UC4) were conducted at various test sites and under various climate conditions (Australia, Portugal, Sweden) for more than 7 years and confirmed results of laboratory testing. Independent of the climate conditions DMDHEU treated Scots pine was classified as ‘durable to very durable’ (DC1 - 2). Contrary, high variations were detected within the durability classifications (‘very durable to not durable’) of treated beech wood and may be related to a poor treatment quality of beech wood, rather than less potential of the DMDHEU treatment itself to improve biological durability of wood (Emmerich *et al.* 2018). In the marine environment (UC5), DMDHEU treatment was graded with the highest durability class DC D ('durable') at various treatment levels and under feeding pressure of the shipworm *Teredo navalis* (Klüppel *et al.* 2012). Termite feeding was significantly reduced compared to untreated wood samples what was proved during laboratory (Gascón-Garrido *et al.*2013) and field testing (Militz *et al.* 2011).

Weathering performance

Lignin was found to be photostabilized to some extent by treatment at high *WPG* levels (> 25 %). Photodegradation of cell wall components, especially cellulose, is slowed down, illustrated by reduced tensile strength losses caused by weathering. Discoloration and greying of modified wood surfaces, caused by colonization of blue stain and moulds, appeared time-delayed but were still apparent. However, penetration of staining fungi was found to be more shallow compared to untreated wood. Weather-induced surface erosions, deformations and crack formation were reduced in the long-term (Xie 2006). In contrast to the long-term weathering performance, an increase in crack sensitivity was recognized for DMDHEU modified wood under changing moisture conditions at the beginning of outside exposure (Emmerich 2016). This was attributed to an anisotropy concerning the modified material´s stiffness and a decrease in plastic deformability, related to the dense and stiff three-dimensional network inside the wood matrix, created by DMDHEU molecules (Bollmus 2011). However, this is not the case for modified and coated material where after a seven-year outdoor weathering the appearance (cracking and staining) did not obviously change and service lives of coating systems were shown to be extended (Xie *et al.* 2014).

Moisture behaviour

Shrinking and swelling were reduced significantly by a permanent *bulking*. As a function of wood species, used chemical reagent, catalyst and applied concentration, a permanent anti-shrink efficiency (*ASE*) of up to 70% was achieved (Militz 1993, Krause 2006, Bollmus 2011). At high relative humidity (*RH*) the equilibrium moisture content (EMC_R, wood cell wall moisture content) and generally water vapor adsorption were reduced by DMDHEU modification (Bollmus 2011, Emmerich 2016). Even water uptake and *FSP* (reached at *RH* < 100 %) were reduced by DMDHEU treatment (Wepner 2006).

Mechanical properties

Strength properties of wood modified with DMDHEU were affected in different ways. Surface hardness (Brinell) rose at high-level with increasing *WPG*. Comparable correlation arose between *WPG* and compression strength, whereas *vice versa* correlation was found for work in bending and tensile strength (Krause 2006, Bollmus 2011). Bending strength and modulus of elasticity (*MOE*) were almost unaffected (Schaffert 2006, Bollmus 2011). Nevertheless, deformation properties were affected by the wood-polymer-matrix created by cross-linking cell wall polymers and DMDHEU molecules, affecting stress-strain behaviour as plastic deformability significantly decreases. As key parameters for the brittleness of a material, dynamic mechanical properties such as impact bending strength and structural integrity decreased significantly by the modification and increased with rising *WPG* (Bollmus 2011, Brischke *et al.* 2012, Emmerich 2016).

More detailed information and further material characteristics e.g. the combustion behaviour, glue-ability and coat-ability of DMDHEU treated wood had been investigated and results of corresponding studies recently summarized by Emmerich *et al.* (2017).

RECENT RESEARCH ACTIVITIES

In 2016 a new cooperation project arose between the University of Goettingen (DE) and the Archroma Management GmbH (Reinach, CH) that acquired the global textile chemical business of BASF in 2014. Thus, recent research activities in Germany focus on formaldehyde-reduced and formaldehyde-free cross-linking agents from textile and paper applications that might suit for modifying wood and lead to the same property improvements as DMDHEU. The focus of this project is either to forward market launch and further, improve the performance of wood modified with corresponding cross-linking reagents. In this context, the following research needs and challenges had been identified:

- Transfer of DMDHEU modification technology to further wood species
- Reduction of the brittleness and susceptibility of uncoated wood to cracking
- Investigations on real-time curing behavior of adhesives and coating systems
- Compatibility of cross-linking agents with further water-dilutable additives e.g. flame retardants, water-repellent agents and fixing agents that might reduce leaching of formaldehyde-free cross-linking resins

Currently, upscaling of DMDHEU treatment for Radiata pine is running in New Zealand (NZ) and led to promising prospects to make DMDHEU treatment a commercial reality in NZ and Australia (Derham *et al.* 2017). Besides, interest from the wood working industry in Europe (mainly: DE, CH, NL) and Brazil is increasing strongly and individual projects based on various innovative product ideas had been started focused on indoor as well as outdoor applications.

CONCLUSIONS AND OUTLOOK

Wood modification with DMDHEU has a high commercial potential. It was confirmed as an environmental benign and promising technology to make wood species with low natural durability applicable in outdoor areas by a considerable and permanent enhancement of the dimensional stability, surface hardness and biological durability. The suitability of impregnation and kiln plants, already well-known in the wood working industry, reduces market entry barriers significantly. Since water is used as solvent within the impregnation solution, this simplifies the impregnation process and makes this technology of interest also for smaller and medium-sized companies.

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Architects perception of modified wood: a parallel study in selected countries of Europe

Manja Kitek Kuzman[1], Eva Haviarova[2], Dick Sandberg[3]

[1]University of Ljubljana, SI-1000 Ljubljana [email: manja.kuzman@bf.uni-lj.si]
[2]Purdue University, USA- 47905 IN Lafayette [email:ehaviarova@purdue.edu]
[3]Luleå University of Technology, S-93131 Skellefteå [email: dick.sandberg@ltu.se]

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ABSTRACT

Nowadays, a wide variety of engineered wood products (EWPs) are available on the market, but many of these EWPs are still underutilized. The market for new durable products of modified wood has increased substantially during the last few years. Wood modification is implemented to improve the intrinsic properties of wood and widen the range of timber applications, and to acquire the form and functionality desired by engineers, without jeopardizing the environmental friendliness of the material. To better understand this situation, a global research project has been undertaken in selected countries of Europe and selection regions in the United States to determine how architects specify EWPs in their profession. Results suggest that, generally, there is a positive perception regarding the use of wood in all countries. The study provides an updated overview of the perceived identity of modified wood products among the architects. The perception of thermally modified wood (TMW) is positive. Differences were found in perceptions of EWPs, the importance of timber-based construction and the markets bio based materials. Our findings suggest that as environmental attitudes evolve in society and a greater proportion of consumers search for environmentally friendly product alternatives, the opportunities for wood to gain market share will increase.

INTRODUCTION

During the 2000s, increasing pressure to find balance in utilization of wood-based forest resources, to enhance economic, environmental, social, and cultural benefits have emerged at the local, regional and national levels (Dargush *et al.* 2010, Lähtinen, T. Myllyviita, 2015). In this context, wood has since decades been developed to form a range of products that are increasingly functional, and based on a combination of performance and sustainability requirements. This has been possible because of new industrial processes, which extend the dimensions beyond the size of the log and modify the properties of natural wood, as well as the need to utilize manufacturing residues and lower grade trees to produce more versatile and consistent products. The result is a vast array of materials, known as engineered wood products (EWPs), ready to be use in contemporary architectural designs and building applications (Sandberg 2016, Jones and Brischke 2017) (Table 1).

EWPs, which are also referred to as reconstituted wood, wood-based products, wood-based composites or man-made wood, are among the most important, innovative wood products used today worldwide. EWPs are in general structural and non-structural components used for interior and exterior applications, industrial or non-industrial, in production of furniture, in the buildings construction, and in infrastructural timber constructions such as bridges, towers, and pathways. The base of an EWP is usually sawn timber, veneer, wood strands, chips or fibres, which are bounded with adhesives, resins or plastic to appropriate structures and shapes. EWPs are gradually and successfully replacing classical building materials such as metal, concrete, and bricks

Table 1: Only recently has wood been utilized to form a range of products that are increasingly functional, based on a combination of performance and sustainability requirements. The result is a wide range of materials, known as EWPs, available for contemporary architectural design

GLT Gluelam - glued -laminated timber	**CLT** Cross-laminated timber	**PSL** Parallel strand lumber	**LSL** Laminated strand lumber	**LVL** Laminated veneer lumber
				
SWP Solid wood panel	**PB** Plywood board	**LDF/MDF/HDF** Low/medium/high-densit fiberboard	**VP** Veneered particleboard	**PB** Particleboard
				
OSB Oriented strand board	**LS** Light sandwich (honeycomb) panels	**WPC** Wood plastic composites	**TM** Thermally modified wood	**WFI** Wood fibre insulation boards
				

Their advantage is in their high load-caring capacity in relation to their weight, their dimensional stability, and their flexibility for adaptation to the required shapes and dimensions of the structural element. EWPs have in general more consistent properties in their planar directions and in the cross section of the composite, and the safety margins in strength can be narrower than those required when sawn timber is used.

The market for EWPs including so-called "modified wood" has increased substantially during the last few years, especially in Europe. This increased interest depends partly on the restricted use of toxic preservatives, due to an increased environmental concern, and partly on the need for low maintenance products. This new type of wood modification is realized to improve the intrinsic properties of wood, to widen the range of timber applications, and to acquire the form and function desired by engineers, without affecting the environmental friendliness of the wood material. That means that e.g. traditional preservation chemicals including toxic substances should not in that sense be used to modify wood for the use in EWPs.

An ongoing study (Goli and Todaro 2018) of the use of modified wood in Europe shows that the dominating wood modification method in Europe is thermal modification. Modification methods to create resin-impregnated and resin-densified timber or veneer also exist on the market for decades, but only as a low volume niche products. Two "new" industrial wood modification methods were recently introduced; furfurylation and acetylation, and these products gain increased interest on the market.

The volumes of modified wood are still small compared to the volumes of sawn timber produced. Europe globally dominates the production of modified wood, with the annual production of thermal modified timber about 400,000 m^3, of furfurylated timber about 25,000 m3, and of acetylated timber about 45,000 m^3. Thermal modification has also increased industrial interest outside of Europe, e.g. North America, with an estimate of the global annual production of 600,000 m^3 of thermal modified timber.

The introduction of new products in the construction sector is generally met with low awareness and high uncertainty (Malaval 1998, Robichaud 2009). Several studies have contributed to the understanding of the market for timber as a structural material in multi-storey buildings by studying e.g. actors' awareness and perceptions, hindrances and drivers for adoption, and innovation diffusion, see e.g. (Bysheim and Nyrud 2009, Hemström *et al.* 2011, Thieger *et al.* 2017). Some researchers have focused on a specific EWP (Mallo and Espinoza 2013). Less focus has been placed on the use of EWPs other than for structural purposes. Nevertheless, some studies have been made of e.g. consumer acceptance of wood-plastic composites (Osburg *et al.* 2016) and professional adopters perceptions of thermally modified wood (Gamache *et al.* 2017). The majority of these studies are descriptive and only Bysheim and Nyrud (2009) and Hemström *et al.* (2011) focus on the relative importance of factors believed to influence the material selection, and only (Mallo and Espinoza 2015, Osburg *et al.* 2016, Gamache *et al.* 2017) focus explicitly on EWPs. A number of studies have been conducted on barriers and challenge of the increasing use of wood in the non-residential sector, with a particular focus on wood as a structural material (Kozak and Cohen 1999, Kozak and Cohen 2007, O'Connor 2004, Robichaud *et al.* 2009).

OBJECTIVE

To date, the literature is lacking studies that specifically provide a comprehensive understanding of architect perceptions related to EWPs. As such, we selected architects in Slovenia, Austria, France, Sweden, Croatia, Bosnia & Herzegovina (BiH) as the target group for this research effort, as they are key decision makers in the selection of materials in the construction sector. Their perception of wood and EWPs as building materials is therefore of great importance, if non-renewable and fossil-based building materials are to be replaced or complimented by wood and EWPs.

This survey is a part of a research project that examined under-utilization of bio-based building materials in the construction of non-residential buildings. The study provides a preliminary assessment of their potential usage by architects in practice, based on their attitudes to the use of wood in non-residential construction.
As part of this project, a preliminary study of architects' perception of modified wood is provided.

The specific goals of the study were:

(1) to identify the use of modified wood in architectural planning, and
(2) to clarify the architects´ knowledge of modified wood and its advantages.

MATERIALS AND METHODS

A survey questionnaire was developed by an international group of architects. These participants had broad expertise in the wood products sector, including architecture, wood technology and construction. The methodology included a two-stage survey. In the first stage, personal interviews with a selected group of architects from the architect's professional organization were conducted. Based on the information given by these in-person interviews, an exploratory web-based survey was subsequently designed (Fleming and Bowden 2009). In the second stage, data from a broader community of architects were collected by the on-line survey (Dillman 2000).

The target population of the survey included practicing architects, targeted through members of professional architect's associations: in Slovenia, Austria, France, Sweden, Croatia, BiH. Respondent data were collected by the on-line survey. An e-mail list for each architect's association was available and random sample of these association populations was used. Based on similar studies (Kozak and Cohen 1999, O'Connor *et al.* 2004, Hemström *et al.* 2011), a response rate of about 30 percent was expected. The survey process took place from November 2016 to January 2017. Two e-mail survey reminders followed the initial mailing. The first reminder was sent one week after the original mailing and the second, two weeks after the first reminder. The statistical software SPSS 21.0 was used for data analysis. The Fisher's Exact Test was applied to compare the results between countries.

RESULTS AND DISCUSSION

About 90% of all respondents work with architecture, followed by 5% of respondents working with building construction, while the remainder work in project management, interior design and structural engineering. Respondents had an average of 15-25 years of experience in Slovenia, Austria and France and 5-15 years of experience in Croatia, BiH and Sweden. In Slovenia and France 50% of respondents were men and 50% women, in Croatia 46% of respondents were men and 54% women, 45% of respondents from BiH were men and 55% were women and in Sweden 56% were man and 44% woman.

Increased use of new EWPs

Respondents were asked if they think there has been an increased trend in use of new EWPs in the last 5 years (Figure 1). 88% of Slovenian respondents stated that they think that use has increased, and 13% stated that the use remained the same. 33% of Croatian respondents believed that the use of EWPs increased, while 48% think that it remained about the same. In BiH 55% think that use increased, and 40% that it remained the same. 6% of respondents from Croatia and BiH think that the use decreased. In Austria 90% think that the use has increased, while in France and Sweden it is 70%.

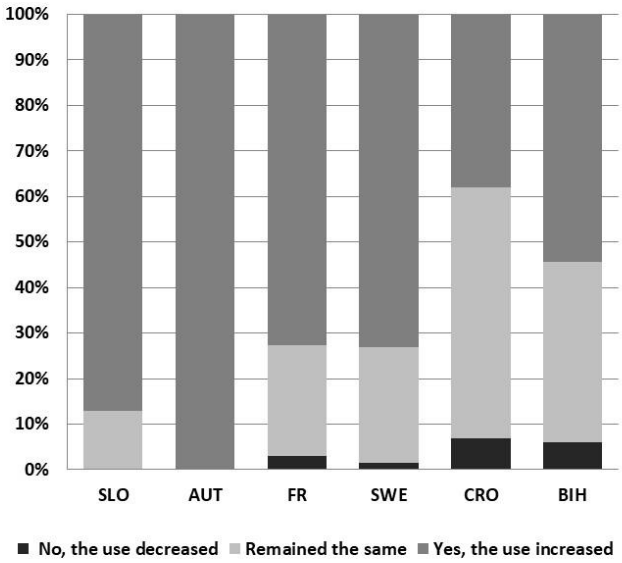

Figure 1: In your opinion, is there increased use of new EWPs in your country in the last 5 years?

Use modified wood in Architectural design

Respondents were also asked if they use modified wood in their architectural design. Almost 65% of Slovenian and Austrian architects use modified wood, as well as 50% of Swedish architects. Data are different for Croatia and BiH; in Croatia about 30% architects use modified wood and in BiH a bit more than 40% (Figure 2).

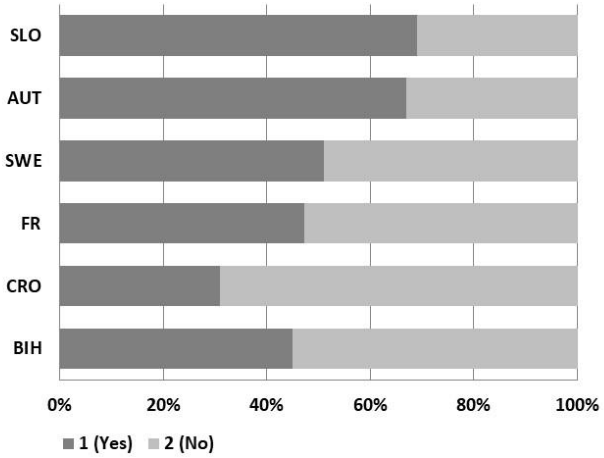

Figure 2: Do you use modified wood in architectural design?

Familiarity with modified wood's advantages

Respondents were next asked if they are familiar with advantages of modified wood. Most of architects in Slovenia, Austria, Sweden and France are familiar with modified wood advantages and they reported: increased durability and stability of wood, modified wood results in a beautiful brown colouration, it is possible to use timber resources that are underutilized, modification is environmentally friendly, but there is a high cost of modified wood. Croatian and BiH architects are less familiar with modified wood advantages and they would be interested to have more information and collaborations with providers of thermally modified wood (Figure 3).

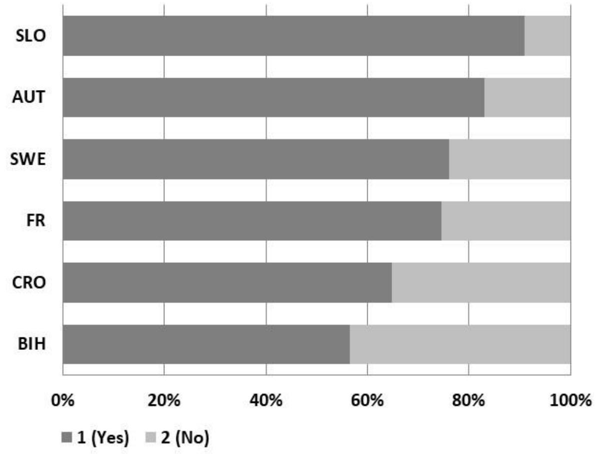

Figure 3: Familiarity with modified wood's advantages?

Information sources and needs of architects / promotional methods

Given the importance of learning about products on the job, respondents were queried about various methods how to obtain information at work. Selections were made based on the following list of promotional methods: Internet, from building companies, through EWPs manufacturers, through architect associations, and homeowners. The respondents were asked to select a number from 1 to 3, where 1 reflected the information source was not important, while 3 indicated that it was important. As seen in Figure 4, the average values for all countries are presented. In all countries, the most important informational tool is the Internet, followed by building companies and EWPs manufacturers.

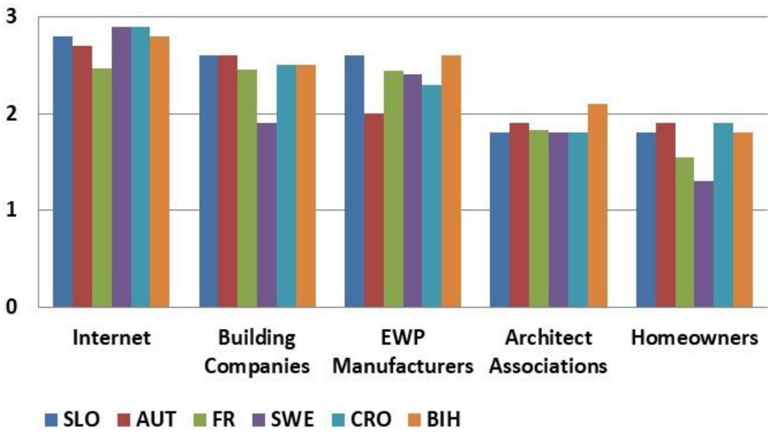

Figure 4: Importance of various information sources: 1-Not important and 3- Important.

Respondents were also asked about the effectiveness of various information sources in terms of learning about wood and wood products. Specifically, they were asked to identify ways that they would like to get information about EWPs, through 1) technical specifications; 2) visits to build objects; 3) visits to building sites; and 4) direct contact with manufacturers. Respondents in all countries noted that obtaining information through technical specifications was the top rated preference, followed by visits to building sites (especially in Slovenia) and visits to build objects (Figure 5). The last place was through direct contact with manufacturers. Each of these methods is approximately equally influential. However, a few notable differences could be observed.

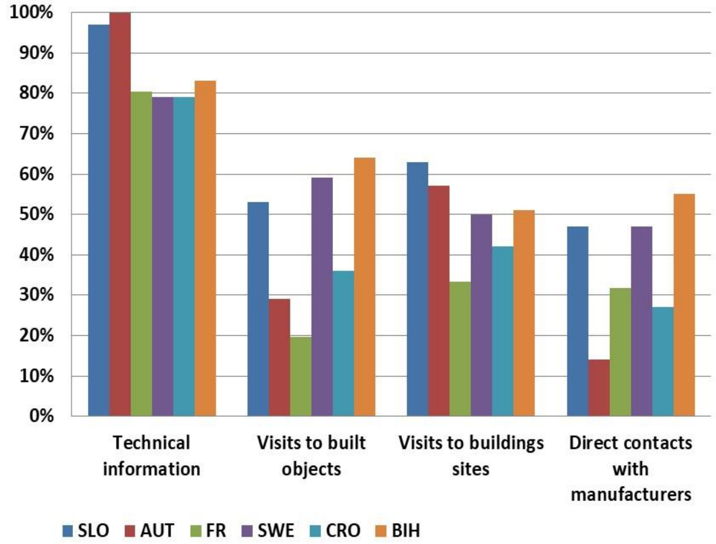

Figure 5: Information needs for EWPs.

CONCLUSIONS

The study provides an updated overview of the perceived identity of modified wood products among the architects. Results suggest that in general, there is a positive perception regarding the use of wood in all countries. The perception of thermally modified timber (TMT) is also positive, while the more recently introduced modification methods on the market, such as acetylation and furfurylation, are not well known. Differences were found in perceptions of EWPs, the importance of timber-based construction, and the markets for bio based materials.

Using information obtained in this and similar studies, region-specific promotion campaigns could be developed with the aim to increase the use of modified wood in various applications. Long-term cooperative programs, multidisciplinary approaches, including lobbying efforts and promotional campaigns, are needed to ensure that material specifiers have the knowledge and training to use traditional and new wood products that are ideally suited for the building sector.

ACKNOWLEDGEMENTS

The authors would like to thank COST FP1407 and Slovenian Research Agency (P4-0015) for financial support. Financial support from the Swedish Research Council Formas (projects EnWoBio 2014-172 and Experimental studies of capillary phenomena in bio-based materials 942-2016-64) is also gratefully acknowledged.

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Enhancing the Properties of ThermoWood® with Phenolic Resin Treatment

Reeta Stöd[1], Janne Pynnönen[2], Duncan Mayes[3] and Bodo Caspar Kielmann[4]

[1]Stora Enso Wood Products Oy Ltd, P.O. Box 309, FI-00101 Helsinki, Finland
[email: reeta.stod@storaenso.com]
[2]Stora Enso Wood Products Oy Ltd, P.O. Box 309, FI-00101 Helsinki, Finland
[email: janne.pynnonen@storaenso.com]
[3]Stora Enso Wood Products Oy Ltd, P.O. Box 309, FI-00101 Helsinki, Finland
[email: duncan.mayes@storaenso.com]
[4]Georg-August-Universität Göttingen, Büsgenweg 4, DE-37077 Göttingen, Germany
[email: bodo-caspar.kielmann@forst.uni-goettingen.de]

Keywords: Phenolic resin, ThermoWood®, impregnation, weathering, water absorption, dimensional stability, natural durability

ABSTRACT

Along with the growing construction industry, the demand for long-lasting, low-maintenance and sustainable building materials is increasing. ThermoWood treated with phenolic resin (PF) might offer an alternative to substitute other materials, such as tropical hardwoods in outdoor construction, or artificial construction materials in residential and other buildings. One potential end use application for PF treated ThermoWood is as exterior cladding, where the long durability in use makes it a sustainable choice. The PF treated ThermoWood offers several benefits as improved product properties. Firstly, resin treatment has been noted to markedly improve the weather resistance of ThermoWood. The effect was shown by the accelerated weathering tests as well as by natural weathering in the outdoor exposure. In addition, the treatment improved water repellency and effectively protected the wood against biological degradation. Thus, the results indicate that phenolic resin treatment may be used to enhance the critical properties of ThermoWood to guarantee longer maintenance intervals and durability in use for the high-quality end products.

INTRODUCTION

Wood modification aims at compensating the undesirable properties of wood, such as the sensitivity to decaying fungi, UV and moisture. At the same time, modification should not affect negatively the good, natural properties of wood, and should not harm either the environment or the users. Despite the wide range of different modification methods available, no method has shown any clear advantages over the others. Thermal modification, for instance, improves the dimensional stability and decay resistance of wood, but simultaneously results in decreased strength values.

Combining modification methods and thus adding product value was tested in this study. The objective of the development was to produce materials with good dimensional stability, as well as resistant against fungi, moisture, and weathering.

The aim of the present study was to determine the properties which affect the maintenance intervals and durability of the final products in the long-term use in varying conditions. The studied properties were weather and water resistance, dimensional stability and natural durability of phenolic resin treated wood. Based on the material properties, the possibilities to produce high-quality, value-added products were evaluated.

EXPERIMENTAL

Material

The raw material for the study was collected from industrial production, including the quality control of raw materials and end products. Scots pine (*Pinus sylvestris* L.) sawn timber was thermally treated according to the standardised ThermoWood® processes into Thermo-D, at 212°C.

The phenolic resin treatment of wood was done using pressure impregnation. The aim of trial impregnations was to study, for instance, the applicability of different phenolic resins to the treatment of ThermoWood, the optimal retention and behaviour of resins in different processes, as well as the shelf and service lives of the resins. In this study, the curing step of treatment process was also under development.

The material from successful processes, i.e. from those which could be repeated in the industrial scale, was utilized to prepare the test specimens. The specimens did not originate in one specific process, and there was also variation in the phenolic resin used, as well as in the chemical retentions. The non-treated ThermoWood and natural pine were included into the tests as reference materials. The preparation of test samples followed the corresponding European and ISO standards.

Methods

Weathering

The natural weathering of wood was tested according to the in-house standard of the laboratory responsible for the testing. The test set up with no eaves or other protection from the weather conditions was as presented in Figure 1. The outdoor weathering test included the visual evaluation of the cladding panels in the beginning of the test. The number and width of checks and other defects were evaluated once a year.

Figure 1: Exterior cladding test set up at Georg-August-Universität Göttingen in Germany.

The artificial weathering test was done in a climate chamber following the standard ISO 11341 (International Organization for Standardization 2013) (Table 1). The duration of a weathering cycle was two hours, and the cycles were repeated until achieving the total exposure time of 1,200 hours. The artificial weathering of 1,200 hours in the climate chamber corresponds roughly to two years of outdoor exposure in the Nordic climate conditions.

Table 1: Exposure cycle phases in the artificial weathering test using daylight filters.

	Exposure period [min]	**Exposure**	**Narrowband irradiance [W/(m²·nm)]**	**Black-panel temperature [ºC]**	**Chamber air temperature [ºC]**	**Relative humidity [%]**
Phase 1	18	Water spray	0.51	55	38	50
Phase 2	102	Dry	0.51	55	38	50

The CIELab colour coordinates (lightness=L^*, red-green=a^*, yellow-blue=b^*) of the test specimens were measured in the beginning of the weathering test and at the intervals of 200 hours until achieving the total exposure time of 1,200 hours. The colour changes (E_{ab}^*) from one measurement (1) to the following (2) were determined, and based on them, the total colour change (ΔE_{ab}^*) was calculated as follows (Eqn. 1):

$$\Delta E_{ab}^* = \sqrt{(L_2^* - L_1^*) + (a_2^* - a_1^*) + (b_2^* - b_1^*)} \qquad (1)$$

Water absorption

The water absorption of wood was determined according to the standard EN 927-5 (European Committee for Standardization 2007). The test for water absorption included pre-conditioning of the samples followed by 72 hours' absorption cycle, during which the end-sealed samples were floated face down in the water. The maximum water absorption (MWA) was calculated as grams per square meter.

Dimensional stability

The test specimen dimensions were measured according to EN 13647 and the dimensional stability, i.e., the cumulative relative change (d_{cr}, %) of dimensions, was defined following the standard EN 1910:2016 (European Committee for Standardization 2012, 2016). In the standardized test, the specimen dimensions were measured after conditioning (RH 65±5%, T 20±2 ºC) and after stabilization in the dry (RH 30±5%, T 20±2 ºC) and in the humid (RH 85±5%, T 20±2 ºC) climates.

Natural durability

The natural durability of wood was determined according to the standard EN 113, including the accelerated ageing prior to the test according to the EN 84 (European Committee for Standardization 1997).

RESULTS AND DISCUSSION

Weathering

Both natural and artificial weathering indicated that the phenolic resin treatment improved the weather resistance of wood. The visual evaluation of the outdoor test elements indicated markedly lower tendency and severity of checking for PF-treated ThermoWood than for the non-treated wood. The PF-treated wood had maintained its original, brown colour during the twenty months' follow-up period, whereas the colour of non-treated reference had changed into grey (Figure 2).

The positive effect of phenolic resin on the colour stability of ThermoWood was noted also in the artificial weathering test (Figure 3). Especially the change in lightness was markedly higher for the non-treated ThermoWood.

Figure 2: Non-treated ThermoWood reference (upper) and PF-treated ThermoWood (lower) outdoor weathering test elements after twenty months of outdoor exposure in Germany.

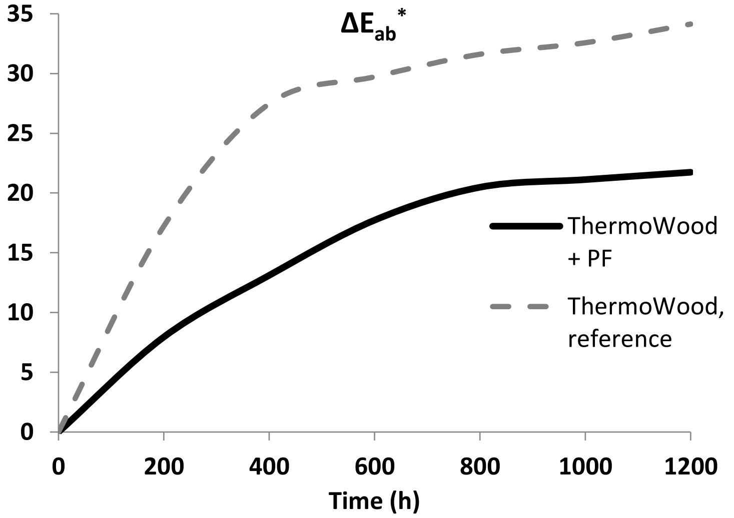

Figure 3: The colour change (ΔE_{ab}^*) of non-treated ThermoWood reference and PF-treated ThermoWood during the 1,200 hours' artificial weathering test.

Water absorption

As expected, phenolic resin markedly improved the water repellence of wood. The maximum water absorption value (MWA) was 850 g/m^2 for untreated ThermoWood and 203 g/m^2 for phenolic resin treated ThermoWood. In comparison, the MWA of untreated pine was as high as 1,280 g/m^2.

Dimensional stability

The cumulative relative change (d_{cr}) of width was noted to be somewhat higher for untreated ThermoWood than for the combination of ThermoWood and phenolic resin (Figure 4). Where the thickness was concerned, a larger difference between the studied wood qualities was noted. In comparison, for untreated pine the d_{cr} of width was 1.9% and that of thickness 2.3%.

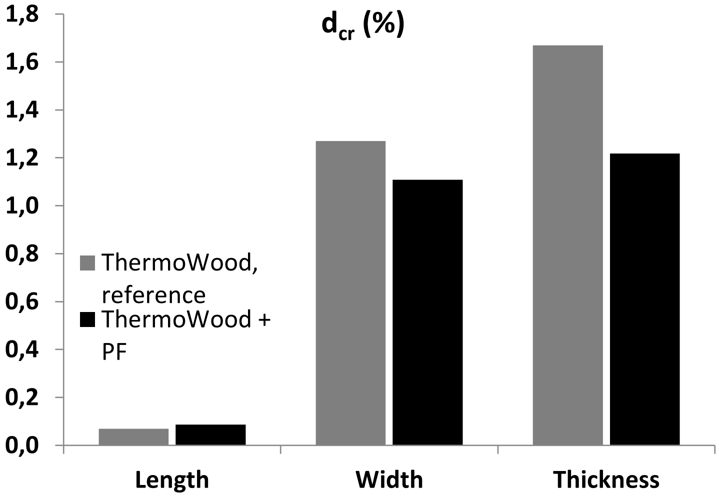

Figure 4: The cumulative relative changes (dcr, %) of length, width and thickness of non-treated ThermoWood reference and PF-treated ThermoWood.

Natural durability

Like in several previous studies, the non-treated ThermoWood was noted naturally durable against the selected decaying fungi (Table 2). Impregnation with phenolic resin improved the resistance of ThermoWood against the biological deterioration so that it achieved the durability class 1, thus being classified as very durable.

Table 2: Natural durability classification of non-treated ThermoWood reference and PF-treate ThermoWood according to the EN 113 standardised test.

	Mass loss [%]	**X-value (EN 350-1)**	**Durability class**	**Highest mass loss fungus**	**Visual grade**
ThermoWood + PF	4.51	0.12	1 (Very durable)	*Poria Placenta*	1
ThermoWood, reference	8.18	0.30	2 (Durable)	*Poria Plancenta*	2

CONCLUSIONS

This study summarized the test results concerning the properties of ThermoWood treated with phenolic resin. The trial treatments showed that the optimal chemical retention may be achieved by the means of pressure impregnation, and that the curing step is an essential part of the process, especially in the industrial scale.

Applying phenolic resin treatment for ThermoWood improved the weather and water resistance of wood, and consequently, increased also the dimensional stability. Thus, the combination of ThermoWood and phenolic resin may bring notable benefit in exterior use, such as in claddings.

In addition, the study indicated that the phenolic resin treatment improves the natural durability of ThermoWood, and may result in very durable wood material. However, this is to be confirmed by a long-term field test before recommending the said product for more demanding ground contact conditions.

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SESSION THREE

Poster Session 1

Effect of Thermo-Mechanical Treatment on Properties of Parica Laminated Veneer Lumber (*Schizolobium amazonicum* Huber ex Ducke)

Mírian de Almeida Costa[1] and Cláudio Henrique Soares Del Menezzi[2]

[1]Universidade de Brasília. Brazil [email: almeida.mira@gmail.com]
[2]Universidade de Brasília. Brazil [email: cmenezzi@gmail.com]

Keywords: Densification, LVL, Parica

ABSTRACT

Physical and mechanical properties of LVL made of *Schizolobium amazonicum* (Parica) veneers that was densified at the moment of manufacture were investigated. The FF panels were pressed for 20 minutes at 150°C in three different press levels – 1.0, 1.47 and 2.94 MPa – characterizing the untreated samples, treatment 1 and treatment 2 respectively. The results showed that physical properties (thickness swelling, water absorption, springback) were higher for treated LVL. Besides, the densification at the pressing time caused positive effect on mechanical properties (rupture and elasticity moduli, Janka hardness and glue line shear), but none of them statistically significant.

INTRODUCTION

Schizolobium amazonicum, known as parica, proved to be an excellent alternative from a silvicultural perspective; due to its commercial value and fast growth, this specie presents great potential in reforestation programs and agroforestry systems (Pereira *et al.* 1982, Vibrans 1996, Rosa 2006). Moreover, parica yields wood with favourable technological characteristics to produce veneers and wood panels (SBS 2017), which have been explored by wood industries in the Northern region of Brazil.

Limitations related to fast-growing trees like low density and small-diameter trees are minimized with adhesive bonding technologies at manufacturing reconstituted wood products, as laminated veneers lumber (Iwakiri *et al.* 2010). LVL constitute a product with a high potential to gradually replace structural elements of wood from native species that are still widely utilized in civil construction in Brazil (Bortoletto *et al.* 2004).

Densification is a viable thermomechanic treatment to increase the resistance of LVL produced with low-density species. It occurs by applying heat and mechanic compression in the perpendicular direction to the fibers, and conducted in different combinations of time, temperature and pressure it can increase wood or composite density.

Taking this into account, this paper aims evaluate the effect of different densification strategies on physical and mechanical properties of parica LVL, which were applied during their manufacture.

EXPERIMENTAL

LVL panels were manufactured from 2 mm thick parica veneers and the adhesive used was Cascophen HL-7090 HS, a high moisture resistant phenol-formaldehyde resin. Firstly, the parica veneers were dried to reduce the moisture content to 4-6%. Then they were cut in sections of 250 mm x 400 mm for the later confection of the LVL. Each panel was assembled with 8 veneers randomly selected, which made the panel nonhomogeneous (there was no veneers classification by resistance).

The adhesive was spread at the rate of about 200 g/m^2 on single glue line. A cold pressing was performed previously for 40 minutes to assemble the sheets, and then a hot pressing at 150° C for 20 minutes at three pressure levels (1 MPa, 1.47 MPa and 2.94 MPa), characterizing the three different treatments evaluated. Three panels were prepared for each treatment.

After the treatment time under pressure, it was zeroed and the material was maintained for another 5 minutes in contact with the heated plates. This is a crucial stage in which the compressive stress relaxation occurs, reflecting on dimensional stability of the material. Later, the panels were removed from the press for cooling and acclimatization to proceed with the measurements.

The mechanical properties assessed were: static bending in the perpendicular direction to fibers, obtaining the modulus of elasticity (E_M) and modulus of rupture (f_M) at flatwise position, according to the standard ASTM D5456 (2006); Janka hardness (f_H), as stated in the standard ASTM D1037 (2012) and the glue-line shear strength ($f_{gv,0}$), conforming to the European standard EN 314–1 (2004).

Static bending test was performed in 9 samples from each treatment and controls, with dimensions of 50 × 400 mm and thickness varying according to the treatment. Other samples were taken from these to perform Janka hardness, that were carried out in a universal testing machine (EMIC), with a maximum load capacity of 300 kN.

Specimens of 50 × 50 mm were glued two by two to meet the standard minimum thickness requirement to perform Janka hardness test. Thus, 8 replications were used for each treatment. The glue-line shear strength ($f_{gv,0}$) was performed to assess the influence of treatment on plywood gluing quality using the same universal testing machine and 6 specimens per treatment.

Water absorption, volumetric and thickness swelling tests - obtained in consonance with the standard ASTM D1037, as well as equilibrium moisture content (EMC) were performed by using 10 samples of 50 × 50 mm from each treatment to obtain the hygroscopic behaviour of panels and observe the densification contribution to the dimensional stability.

Compression ratio (CR %), measured after acclimatization, represents the degree of material densification, relating the final to the initial thickness. The higher the CR, the greater the degree of densification.

After swelling and absorption tests, specimens were dried in an oven until constant weight and subsequently the thickness non-return rate (TNRR) was measured. This measure represents the swelling caused by the release of compressive stress during LVL panels pressing. EMC was obtained from the same specimens after measuring TNRR, according to the standard ASTM D 4442 (2003).

RESULTS AND DISCUSSION

Table 1 shows the specific mass (SM) and compression ratio (CR) of LVL panels. SM varied significantly, with averages of 0.41 and 0.46 g/cm^3 for untreated and treated panels, respectively. The results correspond to Zhang *et al.* (1994) and Shukla and Kamdem (2007), which observed the direct relationship between the specific mass and the applied pressure.

Table 1. Specific mass (SM) and compression ratio (CR) of untreated and treated LVL.

Treatment	SM [g/cm³]	CR [%]
Untreated (150°C, 1 MPa, 20’)	0.41 (9.37)	-
T1 (150°C, 1.47MPa, 20’)	0.44 (9.89)	11.21 (46.47)
T2 (150°C, 2.94MPa, 20’)	0.48 (8.57)	25.08 (15.63)
Treatments mean	0.46	18.14

Values in parentheses represent the coefficient of variation (%).

The higher the pressure applied, the higher the CR. Zhang *et al.* (1994) reached the same conclusion when analysing *Populus* LVL. The authors also concluded that the veneers moisture content had a significant influence on the panels compression ratio.

There were no significant differences between the mechanical properties evaluated as stated in the statistical analysis. The average values are inclined to reduce as the applied pressure increases (Table 2). However, unexpectedly, none of the treatments differed statistically from the untreated by the Dunnett test.

Table 2. Mechanical properties of LVL panels.

Treatments	Properties			
	f_M [MPa]	E_M [MPa]	f_H [N]	$f_{gv,0}$ [MPa]
Untreated (150°C, 1 MPa, 20’)	44.52 (19.0)	6118.34 (43.0)	1285.97 (13.0)	2.52 (19.0)
T1 (150°C, 1.47 MPa, 20’)	43.59 (10.0)	4281.27 (14.0)	1412.92 (25.0)	1.99 (49.0)
T2 (150°C, 2.94 MPa, 20’)	42.22 (14.0)	4191.86 (9.0)	1169.76 (7.0)	2.02 (7.0)

Values in parentheses represent the coefficient of variation (%). f_M: Modulus of rupture; E_M: Modulus of elasticity; f_H: Janka Hardness; $f_{gv,0}$: Shearing on the glue line.

In relation to the modulus of rupture (f_M), it ranged from 44.52 MPa (untreated) to 43.59 MPa in treatment 1, and 42.22 MPa in treatment 2, representing a reduction of 2% and 5% respectively. This tendency was also observed in the modulus of elasticity (E_M), since the stiffness values were lower as the pressure increased. The reduction was 30% and 31.5% in treatments 1 and 2, respectively.

Previous works described the moduli of elasticity and rupture reduction after different methods of densification (Bekhta *et al.* 2009, Sandberg *et al.* 2013). Shukla and Kamdem (2007) did not observe any effect of duration of pressure on properties of *Populus* LVL. In contrast, Zhang *et al.* (1994) detected a direct relationship between compression ratio and mechanical properties.

Melo (2012) found average E_M values of 8911 MPa and f_M of 51.26 MPa in LVL produced with previously classified parica veneers and glued with FF adhesive. The author explained that in flatwise laminated systems subjected to bending, the positioning of higher strength veneers near the surfaces makes them more efficient, resulting in laminated composites of higher resistance.

It is noticeable E_M and f_M lower coefficients of variation presented by the treatments when compared to the untreated, which may be an indicator of good adhesion between the veneers after the panel densification. As also observed by Müller (2009), lower variance points to a more balanced distribution of internal tension, when the composition is under bending.

The LVL hardness increased from 1285.97 N (untreated) to 1412.92 N (T1) and reduced to 1169.76 N (T2). This raise in T1 is associated to the increase in the specific mass of the material (Unsal *et al.* 2011), and other authors have observed the same behaviour when working with plywood (Candan *et al.* 2013, Dogu *et al.* 2010). However, when the pressure was increased in 50% of the parica resistance to the compression (T2), there was a tendency to decrease the value of the hardness.

The panels resistance to shear parallel to the glue line ($f_{gv,\,0}$) investigation showed how the increase in pressure did not affect this property either. Shukla and Kamden (2007) used PVAc adhesive to produce LVL made of three species of wood and observed $f_{gv,\,0}$ values ranging from 1.8 to 2.5 MPa.

Table 3 presents the mean and coefficient of variation of the physical properties of the treated and untreated LVL. It is notable that, in general, the increase in applied pressure has led to a decrease in dimensional stability.

Table 3. LVL panels dimensional stability properties.

Treatment	**Properties [%]**					
	TS2h	**TS24h**	**ABS2h**	**ABS24h**	**EMC**	**TNRR**
Untreated (150°C, 1 MPa, 20’)	2.93 (42.0)	4.61 (35.0)	29.00 (18.0)	79.61 (8.0)	13.42 (4.0)	1.93 (10.0)
T1 (150°C, 1.47 MPa, 20’)	7.24* (27.0)	10.38* (20.0)	37.02 (23.0)	91.04 (12.0)	13.45 (11.0)	4.00 (58.0)
T2 (150°C, 2.94 MPa, 20’)	7.18* (44.0)	7.31* (30.0)	37.30* (19.0)	76.57 (15.0)	15.22* (6.0)	4.64 (86.0)

(*) in the same column indicates values statistically different from the untreated by Dunnett test at 5% of significance. Values in parentheses represent the coefficient of variation (%). TS2h: Thickness swelling after 2h; TS24h: Thickness swelling after 24h; ABS2h: water absorption after 2h; ABS24h: water absorption after 24h; EMC: equilibrium moisture content; TNRR: thickness non-return rate.

In relation to thickness swelling after 2 hours, the treated samples swelled by two and a half times the untreated ones, and after 24 hours, T2 had swelled almost 60% more than the untreated, whereas T1 had swollen 125% more. A swelling was expected due to the densified LVL increased compression stress, with greater values as higher the pressure applied. However, no trend was observed as a result of increased pressure.

Water absorption after 2 hours of immersion was similar in T1 and T2, although the Dunnett test considered only T2 statistically different from the untreated. Both treatments were considered statistically equal to the control on water absorption after 24 hours. Melo (2012) obtained similar results with parica LVL, reaching an absorption after 2h average value of 22.58%. Müller (2009) observed a value of 22.68% in the same property in pine LVL. Shukla and Kamdem (2007) investigated LVL made from low-density hardwood and found similar values, varying from 29% to 34%.

Considering the water absorption after 24 hours, the values were very high, even for the untreated samples: while T2 and untreated achieved similar results - 76.57% and 79.61%, respectively - T1 almost doubled its weight by absorbing 91.04%. Melo (2012) found that parica veneers have low specific mass, high porosity and consequently high water absorption capacity. He also observed that parica wood has a high anisotropic coefficient (T/R> 2), indicating that the evaluated veneers are considerably unstable. These findings explain the high values of absorption and swelling of parica LVL, as the elevated coefficient of variation.

Regarding to the EMC, T2 differed statistically from T1 and the control; the low pressure in T1 had no effect on this property. According to Silva *et al.* (2006), in addition to the factors inherent to the wood itself, the type and quantity of adhesive, the time and the temperature of the press influence the panels equilibrium moisture content.

High TNRR materials have greater swelling and thickness expansion. It can be seen from Table 3 that both treatments were statistically equal to the control. The TNRR represents the swelling caused by the stress release, and although statistically equal, treated LVL tended to accumulate the tension more intensely. In bonded materials, the release of the stress compression causes bonding quality loss, thus the quality of the adhesive is important to keep the panel bonded and limit the stresses release (Mohebby *et al.* 2009). Higher values of TNRR also imply reduction of the panel specific mass, since its thickness, after the swelling test and subsequent drying, is increased. This behaviour was observed in T2, whose TNRR was higher, and therefore its specific mass was lower in comparison to T1. It happened because the panels mass is not affected by the swelling test, but the volume increases, reducing its density.

CONCLUSIONS

Due to the release of the compression stress, the thickness swelling, water absorption and the thickness non-return rate were higher in treated LVL, which made them less dimensionally stable. In addition, densification during the pressing process had positive effect on the mechanical properties, however, not statistically significant, regardless of the used pressure.

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TanWood®: The Brazilian Process of Thermal Modification of Wood

Leonardo Puppi Bernardi[1] and Djeison Cesar Batista[2]

1 *TWBrazil* Company, Ponta Grossa, Paraná, Brazil [email: leonardo@twbrazil.com.br]

2 Espírito Santo Federal University, Jerônimo Monteiro, Espírito Santo, Brazil
[email: djeison.batista@ufes.br]

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ABSTRACT

Thermal modification of wood has been scientifically studied for almost one century, although it was industrially consolidated in Europe only on the 1990's, where can be found in operation the most important industrial processes of the world, such as the Finnish ThermoWood® and the Dutch Plato®. The Brazilian company *TWBrazil* started its own research on thermal modification in 2006 and patented a process named TanWood®. The aim of this work was to describe the Brazilian process of thermal modification TanWood® and provide a general comparison to the European ones based on the bibliographic information. TanWood® is a hygrothermal process of thermal modification, which uses saturated steam as heating medium in a pressurized/closed system. TanWood® is similar to the European processes FirmoLin, Moldrup-SSP and WTT ThermoTreat 2.0. For a better comparison between the processes, it would be necessary more detailed information about the European ones, such as the heating system of the equipment used and the processing schedules. More research and development are required for the Brazilian process of thermal modification, in order to improve the equipment and the process, as well as to assess its impacts on the properties of the thermally modified wood.

INTRODUCTION

The Brazilian company *TWBrazil* (Treated Wood Brazil) is located in Ponta Grossa city, Paraná state, Southern Region. It works in the market of wood preservation with waterborne preservatives (eucalypt and pine), wood drying, wood frame, prefabricated wooden structures, fences, and decks.

In 2006, the company started its researches and development about the process of thermal modification of wood, resulting in the Brazilian process TanWood® (former VAPHolzSysteme®) and adopting the name *Thermally Modified Timber* or *TMT* to the products.

Regarding TMT, the company commercializes nowadays mostly teak (*Tectona grandis* L.f). as decks, table tops, garden furniture, wall coverings, and carpets. But tests with other species were already carried out, such as pine, eucalypt and even bamboo culms. The company also produces and commercializes the equipment which does the process.

Nowadays, the process is a reality, and at least six academic studies were carried out about the process (Batista 2012, Bellon 2013, Brito 2017, Griebeler 2013, Lengowski 2011, Menezes 2017).

Literature highlights important considerations about processes comparison (Hill 2006, Homan *et al.* 2000). For example, although thermal modification processes give the same qualitative effects on wood properties (hygroscopicity reduction, increased dimensional stability, and biological resistance), the quantitative effects and the chemical nature of the modifications can be considerably different.

The aim of this work was to describe the Brazilian process of thermal modification of wood TanWood® and provide a general comparison to the European ones based on the bibliographic information.

MATERIAL AND METHODS

The Equipment used in the **TanWood®** *process*

The equipment is constituted basically by i) a steel cylinder/autoclave (pressure vessel) of 125 cm diameter, 850 cm length, with nominal capacity for six cubic meters of wood; ii) an instant steam generator (boiler) class B, with production capacity of 216 kgv.h^{-1}; iii) a water tank; iv) a programmable logic controller (PLC), which controls the variables of the process variables and; v) trails and trams for loading and unloading wood. In a general view, the equipment is similar to those used for wood preservation with waterborne products (Figure 1).

Figure 1: Equipment used in the* TanWood® *process of thermal modification of wood.

Description of the **TanWood®** *process*

Primarily, air-dried or kiln-dried lumber (approximately 15% moisture content) is stacked with stickers of 10 by 30 mm of cross-section and variable length (depending on the position in height) between the layers, and the stack gets the same shape as the cylinder. Stickering permits the steam to flow homogeneously through the lumber inside the cylinder. Figure 2 presents a charge of stacked wood ready to be loaded on a regular business day at the company.

Figure 2: Example of wood being loaded into the equipment.

Figure 3: Color patterns according to the common temperatures used in the **TanWood**® *process. From left to right: untreated, 140 °C, 160 °C, and 180 °C Eucalyptus grandis*

The final cycle temperatures normally achieved by the TanWood® process vary between 140 °C and 180 °C, but tests were already carried out up to 220 °C. Figure 3 presents the different colors of thermally modified fast-grown *Eucalyptus grandis* juvenile wood. TanWood® is divided into five phases and the duration is approximately eight hours with some more eight hours of cooling. A diagram of a theoretical program, with final cycle temperature of 160 °C, is presented in Figure 4, but the pressure is not shown and can achieve from 0.3 to 1.0 MPa in phase four, according to the final temperature.

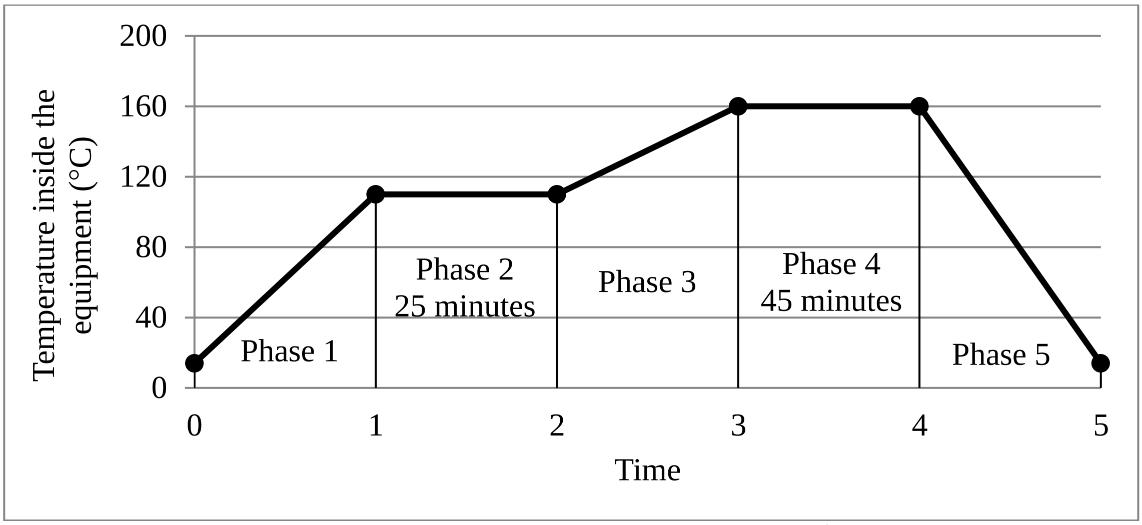

Figure 4: A theoretical example of a typical* TanWood® *process.

The description of each phase follows:

- Phase 1 – Initial heating: corresponds to the beginning of the process after lumber is loaded and the cylinder is closed. Steam is injected inside the equipment and the system is heated up to 110 °C, according to a predetermined heating rate (°C.min^{-1}). The duration of this phase is variable and depends on the heating rate adopted.
- Phase 2 – Constant temperature: after the initial heating, starts the first step of constant temperature, at 110 °C for 25 minutes, so the heating rate is nill in this phase. The goal is drying the wood.
- Phase 3 – Secondary heating: this is the second step of heating, and lengths until the system reaches the final cycle temperature, according to a determined heating rate (°C.min^{-1}).
- Phase 4 – Thermal modification: in this step occurs the thermal modification of wood, and the final cycle temperature is kept constant for 45 minutes.
- Phase 5 - Cooling: after phase 4, the equipment is turned off and the system cools down.

Literature review

Further, a literature review was carried out about the most consolidated and researched European processes of thermal modification of wood which are currently in operation in Europe (Esteves and Pereira 2009, Gérardin 2015, Hill 2006, Militz and Altgen 2014, Rapp 2001, Sandberg and Kutnar 2016, Xie *et al.* 2002).

RESULTS AND DISCUSSIONS

A general comparison between **TanWood®** *and the European processes*

After the description of the TanWood® process, it can be classified as hygrothermal, carried out in a closed system (Hill 2006) or under pressurized conditions (Gérardin 2015). According to the literature review, the Danish companies WTT (Wood Treatment Technology) and IWT/Moldrup develop processes with pressurized conditions (Gérardin 2015, Militz and Altgen 2014). According to Militz and Altgen (2014), the Dutch company FirmoLin Technologies enhanced the process and developed FirmoLin.

We visited the websites of these companies but found little information about the description of the processes (FirmoLin Technologies 2018, IWT/Moldrup 2018). On the WTT's website (WTT 2018), we found a presentation about the process (Klaas 2018) and also have some information directly with Ph.D. Thomas Venås, Director of Sales and New Product Development at WTT. We also found some information about this process in a paper (Dagbro *et al.* 2010). Regarding FirmoLin®, we found its description in the work of Willems (2009) and had some information directly with Ph.D. Wim Willems, the inventor of the process. Regarding Moldrup-SSP, we had the main information directly with Mr. Bror Moldrup.

We present in Table 1 a summary of the main processing conditions of TanWood® and the other closed system/pressurized processes, according to the information we found in the above-mentioned sources. If some information is wrong, the authors take the complete responsibility.

Although the Oil Heat Treatment is a process in a closed system, we did not provide any comparison with it because the wood is immersed in plant oil for thermal modification, making it a very different process from any other currently in operation. The same for Plato®, because only one of its four phases is carried out in pressurized condition (0.6 – 0.8 MPa) (Esteves and Pereira 2009, Militz and Altgen 2014, Rapp 2001; Sandberg and Kutnar 2016, Xie *et al.* 2002). Then we compared only the processes where all the phases are carried out under pressurized conditions/closed system.

The four processes are similar regarding the initial moisture content, where pre-dried wood (10-15%) is demanded in order to avoid drying defects, such as cracks. The temperatures used are similar, around 160 and 190 ºC, lower than the commonly applied in open system processes (Rapp 2001). Processes duration is also similar, ranging from 8 to 24 hours. Lumber thickness and maximum temperature influence on it, but closed system processes tend to be shorter than open system ones, what is an important characteristic to be considered regarding costs ($/m³).

Pressure seems to be higher in the WTT ThermoTreat 2.0 process than in the other three. Final moisture content is higher in the Brazilian process, where for the European ones it ranges from 3 to 7%. Although the equipment seems to be similar for all processes, there is a marked difference between the European ones, because they can have a fan inside the autoclave for steam circulation and homogenization.

Other marked difference in the European processes is the use of an initial pre-vacuum phase. It aims to evacuate the autoclave and the wood from oxygen to ensure the process is carried out in an atmosphere free of air to prevent self-igniting. The vacuum also reduces the boiling point of the water, permitting the use of lower temperatures for drying the water at the beginning of the process.

Table 1: Comparison of the main processing conditions of pressurized processes

Information	Processes			
	Firmolin	TanWood	Moldrup-SSP	WTT ThermoTreat 2.0
Company, country	FirmoWood, the Netherlands	*TWBrazil*, Brazil	IWT/Moldrup, Denmark	WTT, Denmark
Year	2008	2006	1999	2005
Equipment	Two connected pressure compartments: autoclave and boiler	Autoclave	Autoclave	Autoclave
Moisture content (%): initial/final	12/6	12 – 15/13 – 16	10 – 12/3 – 5	10 – 15/5 – 7
Temperature (°C)	160 – 190	140 – 180	Around 180	160 – 180
Process duration (h)	19 – 22	8 – 16	12 – 23 (for 25 mm thickness)	8 – 24
Pressure (MPa)	0.6 – 1.0	0.3 – 1.0	Up to 1.2 MPa	1.4 –2.0
Atmosphere/heat transportation media	Superheated steam	Saturated steam	Wood moisture is transformed in steam through heating by radiators filled with thermal oil	Saturated steam or nitrogen
Remarks	Pre-vacuum (0.01 MPa). Control of the relative humidity through a ratio of 0.75 between the actual steam pressure and the saturated steam pressure at the actual temperature.	Divided into five phases, as described in the Material and Methods.	Pre-vacuum. Radiators (filled with thermal oil) heat the air in the beginning phase; after, moisture evaporated from wood is transformed in steam. If necessary, additional water can be injected in the autoclave for steam production. After the pre-vacuum, pressure and temperature are thoroughly increased until their maximum values. Use of water-mist for conditioning the wood during the process.	Divided into five phases: Pre-vacuum (up to 0.3 bar); Heating (temperature increases up to 110-120 °C); Drying and thermal modification (160-180 °C, for 0.5-1.5 h); Cooling (40-70 °C); Pressure normalization.

CONCLUSIONS

TanWood® is a hygrothermal process of thermal modification, which uses saturated steam as heating medium in a pressurized/closed system.

TanWood® is similar to the European processes FirmoLin, Moldrup-SSP and WTT ThermoTreat 2.0. For a better comparison between the processes, it would be necessary more detailed information about the European ones, such as the heating system of the equipment used and the processing schedules.

More research and development are required for the Brazilian process of thermal modification, in order to improve the equipment and the process, as well as its impacts on the properties of the thermally modified wood.

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Examining the coating performance of finishes on acetylated hornbeam wood (*Carpinus betulus* L.)

Fanni Fodor[1] and Róbert Németh[2]

[1] Institute of Wood Science, Simonyi Károly Faculty of Engineering, Wood Sciences and Applied Arts, University of Sopron, Bajcsy-Zs. Str. 4. H-9400, Sopron [email: fodor.fanni@phd.uni-sopron.hu)]
[2] Institute of Wood Science, Simonyi Károly Faculty of Engineering, Wood Sciences and Applied Arts, University of Sopron, Bajcsy-Zs. Str. 4. H-9400, Sopron [email: nemeth.robert@uni-sopron.hu)]

Keywords: acetylation, coating, finish, colour, glaze, hornbeam, photodegradation

ABSTRACT

The aim of this research was to examine the coatability and colour stability of acetylated hornbeam by using several commercially available oils and glazes with or without pigments. In previous studies, it was found that acetylation – wood modification using acetic anhydride – improves the physical, mechanical, and also the durability properties of hornbeam wood (*Carpinus betulus* L.). Despite these improvements, the colour of acetylated hornbeam is not stable against UV radiation. The dimensional stability of acetylated wood enables that the coating will be less prone to fail (crack) due to moisture sorption. During this one-month-long exposure, it was found that the untreated hornbeam samples cracked, moulded and yellowed while acetylated wood was more durable and dimensionally stable but much less colour-stable. The dark, greyish brown colour of acetylated hornbeam brightened during UV irradiation because of the transformation of extractives and degradation of lignin. The rate of total colour change was much greater in case of coated acetylated hornbeam than coated untreated hornbeam. The best results were obtained using dark pigmented oil and dark pigmented, film-forming glazes. The colourless oil and glazes, as well as the semi-film-forming pigmented oils had similar change of colour like the control samples, here the pigment did not hinder the rate of photodegradation significantly.

INTRODUCTION

When wood is exposed to weather, various physical and chemical changes take place: moisture (precipitation), UV radiation (sunlight), slow or rapid changes in temperature and relative humidity, and biological degradation (wood-decaying fungi and wood-feeding insects).

Moisture can be absorbed by wood from the humid air or from liquid water via the capillary structure. In this case, wood also changes its dimensions in the three anatomical directions, which has a negative effect on the quality and service life of the coating film: the film will swell or shrink differently compared to wood, cracks will form in the film which results in additional dimensional changes, colour changes and biological degradation.

Acetylated wood takes up moisture at a lower rate than natural wood, which makes it a more dimensionally-stable and durable material. The lower shrinking and swelling rate enables a more long-lasting coating film. The higher the WPG (Weight Percentage Gain), the more durable the coating of acetylated wood will be. Wood-decaying fungi can attack acetylated wood as hyphae can be present in its microstructure, but weight loss does not occur or only at a low extent.

The colour change of weathered wood is caused by UV light and visible light up to 500 nm. The main part of photodegradation is due to the photochemical degradation of lignin where demethylation and formation of quinones occur which results in the darkening of weathered wood. The degradation products of lignin are leached out by precipitation which causes the bleaching and greying of the surface.

Although the changes caused by photochemical degradation take place differently in acetylated wood, acetylation does not prevent the colour change of wood – this can be caused by photodegradation as well as mould, blue stain fungi or corrosion of metal fasteners just like in case of natural wood. Blue stain – which is usually black coloured - can be observed on greyed acetylated wood surfaces.

The colour stability of acetylated wood can be improved by using colourless coating systems, and the most stable colour can be achieved by dark, pigmented, film-forming coatings. It is advised to apply multiple coatings. As acetylated wood takes up less moisture, water-based paints penetrate less and form thinner film on acetylated wood. Flaking can be of problem because of increased acidity and buffering capacity. Various case studies have been made in the topic of coating acetylated wood, highlighting the durability of alkyd and acryl coating systems. The maintenance time or service life of coated acetylated wood can be three or four times bigger with appropriate surface preparation, surface treatment and well-chosen coating system (Beckers *et al.* 1998, Schaller and Rogez 2007, Rowell and Bongers 2015, 2017).

The wood species used in this research work is hornbeam (*Carpinus betulus* L.), which is a subsidiary tree species found in Hungary’s hill and mountain forests and it covers about 5.2% of the forest area in Hungary. It can also be found almost all over Europe, from Sweden to Western Asia. The wood of hornbeam is known for its high density, hardness, toughness and wear-resistance, but its poor durability, small yield and low availability of straight, defect-free trunks hinder the usability of this species (and Bariska 2002).

In the work of Fodor *et al.* (2017), it was found that acetylation improves the physical, mechanical, and also the durability properties of this wood species. Despite these improvements, the colour of acetylated hornbeam is not stable against UV radiation, nor weather, nor artificial light (Fodor and Németh 2017). Although acetylation prevented cracking, it was more prone to fade and grey because of UV irradiation.

As a continuation, the aim of this research was to examine the coatability and colour stability of acetylated hornbeam by using several commercially available oils and glazes with or without pigments. As acetylated wood is a natural, nontoxic, biodegradable and aesthetic material, environmentally friendly coatings were used which do not cover up the natural grain pattern of wood.

MATERIALS AND METHODS

Hornbeam boards of 28x160x2500 mm were obtained from Southeast Hungary. Acetylation was carried out under industrial conditions (Accsys Technologies, Arnhem, Netherlands) which resulted in a WPG of 15% for hornbeam.

For the test, samples of 20x20x100 mm were created. The samples were conditioned at normal climate (20°C temperature and 65% relative humidity). The density of the hornbeam and acetylated hornbeam samples were 745 ± 42 kg/m^3 and 795 ± 55 kg/m^3, respectively.

There were various environmentally-friendly coatings applied in this test which are listed below (Table 1). The finishes were applied according to the manufacturer’s instructions (the products were obtained from three different manufacturers: ‘O’, ‘A’ and ‘B’). The spread rate was sufficient in case of both untreated and acetylated wood. Acetylated hornbeam had slightly lower spread rate because of the lower penetrability.

Table 1: Coating of test samples

Sample id.	Manufacturer	Coating type	Color
0	-	None, control	-
OO0	‘O’	Oil	Colourless
AG0	‘A’	Glaze	Colourless
BG0	‘B’	Glaze	Colourless
AOT	‘A’	Oil	Teak
BOT	‘B’	Oil	Teak
BOR	‘B’	Oil	Red
BGR	‘B’	Glaze	Red
AGU	‘A’	Glaze	Umbra
BGP	‘B’	Glaze	Palisander

The samples were mounted on a wooden stand facing south, tilted to 45° and it was arranged on the top of the building of the University Library, this way it was directly affected by the weather without roof or shadow (Figure 1). During the test, colour was measured and changes in the samples were evaluated which were caused by weathering (bleaching, cracking, mould, stain, etc.).

Figure 1: Weathering test of untreated and acetylated hornbeam coated with various oils and glazes, before (left) and after 31 days of exposure (right)

The colour was determined in CIE L*a*b* colour space using Konica Minolta 2600d colorimeter with D65 illuminant and 10° standard observer with a test-window diameter of 8 mm. The colour was measured on tangential surfaces and there were 20 measuring points in case of each type.

The test is carried out continuously, since April 2018. This paper discusses the changes experienced in the first month.

RESULTS AND DISCUSSION

The change of colour coordinates and the total colour change is shown in Figure 2.

As it was experienced in earlier studies (Fodor and Németh 2017), the untreated hornbeam samples were cracked, moulded and yellowed after one month of weathering exposure while acetylated wood was more durable and dimensionally stable but much less colour-stable (Figure 3). During UV irradiation hornbeam yellowed, the red hue (a*) and yellow hue (b*) increased. Discoloration and greying is already present after 1 month. The greying of wood is due to the bleaching of lignin, leaching of water-soluble extractives, which define the colour of wood, and also the photodegradation products, leaving the grey cellulose chains on the surface. The dark, greyish brown colour of acetylated hornbeam brightened during UV irradiation because of the transformation of extractives and degradation of lignin. Unlike hornbeam, its brightness increased while the red and yellow hue decreased.

The rate of total colour change was much greater in case of coated acetylated hornbeam (7.44 … 36.69) than coated untreated hornbeam (1.37 … 10.74). Pigmented oils and glazes had the lowest colour change while colourless coatings had the highest (sometimes even higher than the control itself).

The best results were obtained using red pigmented oil (BOR) and dark, film-forming glazes (AGU, BGR, BGP) (Table 2).

The improvement of moisture and mould resistance was concluded in case of every coating type.

Greying is observed by the reduction of red and yellow hue, which is not observed in case of red pigmented oil (BOR) and dark, film-forming glazes (AGU, BGR, BGP). Here on the other hand, increment or no significant change occurs.

The colourless oil (OO0) and glazes (AG0, BG0) had similar change of colour like the control samples, except the yellow hue decreased in case of hornbeam coated with colourless glazes.

Teak-coloured oils (AOT, BOT) had similar change of colour like the control samples. The pigment did not hinder the rate of photodegradation significantly.

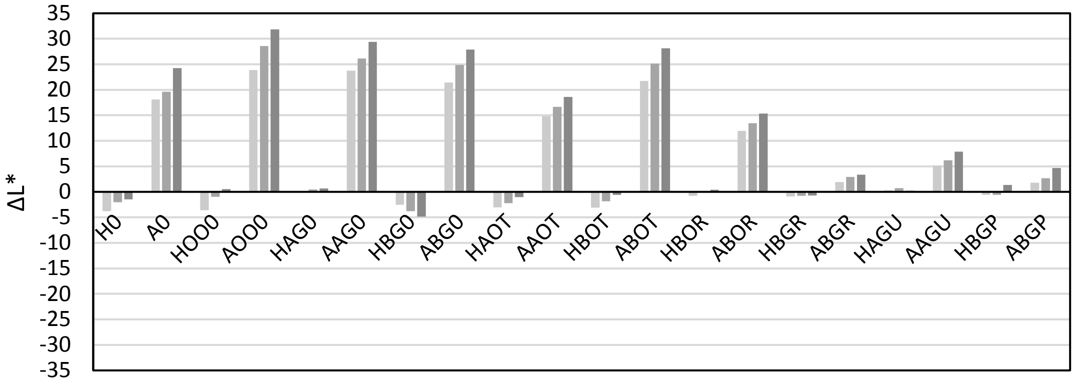
In case of the red pigmented oil (BOR) and the dark, film-forming glazes (AGU, BGR, BGP), weathering resulted in the increase of brightness and red hue, while the yellow hue changed differently for the oil compared to the glazes (Figure 2).

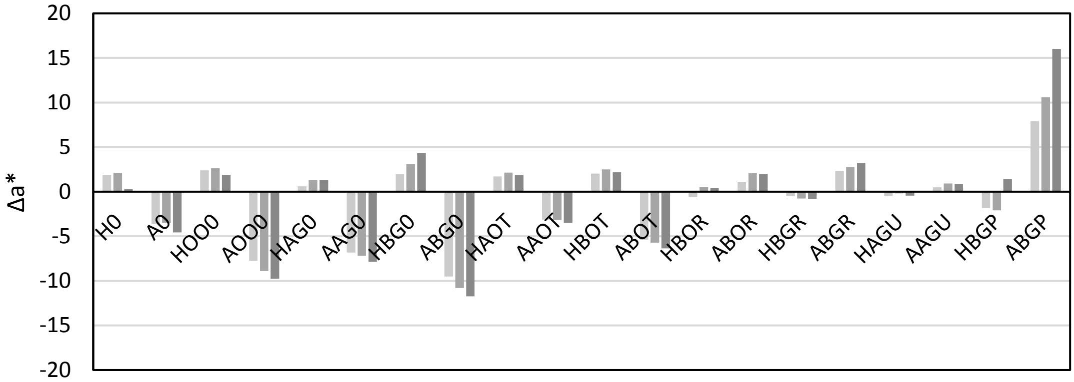
Table 2: Listing coating systems according to colour change

	Hornbeam		**Acetylated hornbeam**	
Colour change (ΔE*) from low to high	BOR	1.37	BGR	7.44
	BGR	1.68	AGU	9.89
	0	2.38	BGP	18.50
	AGU	2.49	BOR	18.59
	OO0	2.92	AOT	19.66
	BGP	3.00	0	25.10
	AOT	3.71	BOT	31.29
	BOT	5.20	AG0	34.51
	BG0	6.52	BG0	36.09
	AG0	10.74	OO0	36.69

OUTLOOK

The consumer expectations of the weathering performance of (modified) wood is a very subjective topic. What is the aim? Should the wood be sealed, covered up in order to be a trendy “natural” material with high durability and stable colour? Should it be stained with natural coatings, showing unique grain structure but with non-stable colour, needing maintenance? Or should we just let it “age with grace” like in the case of “reclaimed wood”? As people tend to expect much better weathering performance from modified wood than natural wood - not just dimensional stability, but photostability -, it is important to give sufficient information about its (unprotected) properties and how these can be improved. Further research and case studies are to be done on this subject, targeting different wood species as well.





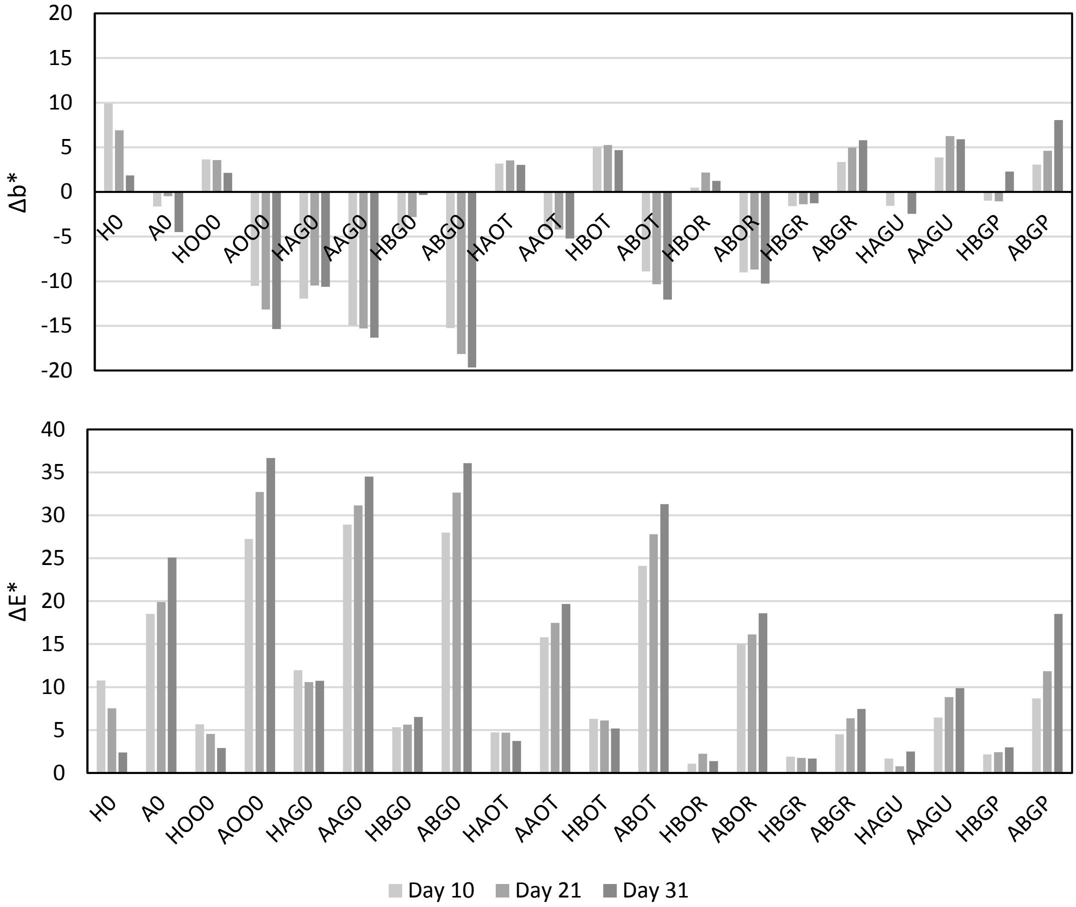


Figure 2: Changes of colour values of untreated and acetylated hornbeam coated with various oils and glazes. ΔL*: brightness; Δa*: red hue; Δb*: yellow hue; ΔE*: colour change.

Figure 3: During the weathering test, untreated hornbeam was cracked and was attacked by mould (left) while acetylated hornbeam remained unharmed (right)

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Colour response of heat treated spruce and pine with different surface coatings in outdoor exposure

Niclas Björngrim[1], Marie Hartwig[2], Olle Hagman[3] and Tom Morén[4]

[1]Luleå University of Technology, Forskargatan 1, 931 87 Skellefteå [email: niclas.bjorngrim@ltu.se)]

[2]Luleå University of Technology, Forskargatan 1, 931 87 Skellefteå [email: marhar-6@student.ltu.se]

[3]Luleå University of Technology, Forskargatan 1, 931 87 Skellefteå [email: olle.hagman@ltu.se)]

[4]Luleå University of Technology, Forskargatan 1, 931 87 Skellefteå [email: tom.moren@ltu.se)]

Keywords: Colorimeter, Heat treated wood, Outdoor test, Thermally modified wood

ABSTRACT

This study is performed primary to study the greying of heat treated wood with different surface treatments and how the different treatments affect the greying process. Secondary aims are to study the durability of the material. The information is useful for architects to help them achieve their desired color on the house façade. In the study 100 boards in four different groups were used. 50 of the boards were of Scots pine (*Pinus sylvestris*) and 50 of the boards were Norway spruce (*Picea abies).* For both the Scots pine and the Norway spruce half of the boards were heat treated with the wood treatment technology (WTT) method and the other half with the ThermoWood (TW) method. From each group five replicates were made; one untreated and four with different surface treatments. The boards were coated with oil, pigmented oil, iron vitriol and a silicon treatment. After treating the boards according to the manufacturer's instructions, the boards were measured with a colorimeter and a hand held NIR device. Lastly the boards were mounted at the site where colorimeter measurements were performed every two weeks until the snow and ice made it unfeasible. The boards were mounted in the end of September 2017. During the spring 2018 the boards were equipped with moisture content sensors which measure the moisture content and temperature every hour. The project will be going on for at least two years, with color and NIR measurements taken twice every month. In this paper color changes for the first ten months is presented.

INTRODUCTION

Heat treated wood has good dimensional stability, resistance to degradation, aesthetics and is sustainable, making it a good choice as a cladding, façade or decking material. However, when wood is exposed to outdoor conditions, changes called weathering can be observed. This is primarily caused by exposure to sunlight but also precipitation, changing temperature and air humidity, abrasion by windblown particulates, contact with biological agents, etc. also affects the degradation of the wood surface (Williams 2005). Weathering is mostly affecting the surface of timber, if there is no decay present. The color, roughness, glossiness of the exposed surface changes over time. This has little impact on the mechanical performance of the structure. However, it alternates the appearance of it, which is e.g. quite important from an architectural point of view. Often the requirements are that the structure does not change the appearance over time, so after setting up a construction the changes due to weathering should be completed rather sooner than later. The change of color is due to degradation of lignin and wood extractives caused by sunlight, especially UV light. The degradation products are then washed out by water leading to a greyish surface. Strong color changes might be reduced by using different treatments to protect the surface or changing the color of the timber already before exposure.

In this project, it is the aim to focus mainly on the color change over time of differently treated timber in an outdoor environment over a long duration. The effect of different treatment on the color change over the exposure time should be compared.

EXPERIMENTAL

In this study 100 boards in four different groups was used. The boards were 3550 mm x 95mm x 28 mm. 50 of the boards was of scots pine (Pinus sylvestris) and 50 of the boards were Norway spruce (Picea abies). Half the boards form each species was heat treated with the WTT method respectively TW method. In the WTT process the boards are heated in an oxygen free atmosphere. The treatment is performed under pressure and at temperatures between 160-180°C (WTT 2018). In the TW process boards are heated in a saturated steam environment at atmospheric pressure. The temperature is 185-212°C (Finnish Thermowood association 2003). From each group five different surface treatments were added; one untreated and four with different coatings. The boards were coated with oil, pigmented oil, Iron vitriol and a silicon treatment. Each coating was applied on five boards. After coating the boards according to the manufacturer's instructions, the boards were mounted at the test site. Color measurements using CIE L*a*b* was performed with a Konica Minolta CR-410 colorimeter according to the CIE standard (Hunt 1995). The color was measured on two locations on each board and with an interval of two weeks.

RESULTS AND DISCUSSION

In Table 1 the average L* (lightness), a* (red-green), b* (yellow-blue) and E (total color change) values with the standard deviation is shown. The calculated color change is from when the surface treatment of the boards had dried compared with ten months of outdoor exposure.

Table 1: Show the difference in color during 10 months of outdoor exposure.

Th. Treat.	Surf. Treat.	ΔL*	Δa*	Δb*	ΔE
WTT^{s}	Untreated	-2.64 ± 1.37	-7.04 ± 0.41	-22.32 ± 1.33	23.59 ± 1.39
WTT^{s}	Oil	1.17 ± 1.29	-9.42 ± 0.46	-14.04 ± 9.82	19.00 ± 4.95
WTT^{s}	Pigmented oil	-1.46 ± 1.12	6.18 ± 0.52	-8.43 ± 3.59	10.82 ± 2.95
WTT^{s}	Iron vitriol	-3.12 ± 1.66	-4.45 ± 0.24	-14.70 ± 1.07	15.76 ± 1.12
WTT^{s}	Silicone based	2.30 ± 3.81	-4.07 ± 1.47	-10.70 ± 4.97	12.09 ± 5.61
TW^{s}	Untreated	-0.69 ± 1.88	-5.76 ± 0.56	-16.22 ± 3.04	17.35 ± 2.97
TW^{s}	Oil	2.45 ± 1.60	-7.51 ± 0.60	-10.54 ± 2.41	13.35 ± 1.96
TW^{s}	Pigmented oil	-0.23 ± 1.23	-5.24 ± 0.58	-7.07 ± 3.72	9.10 ± 3.23
TW^{s}	Iron vitriol	-3.85 ± 2.18	-6.16 ± 0.50	-15.74 ± 2.52	17.46 ± 2.63
TW^{s}	Silicone based	12.22 ± 4.63	-4.84 ± 0.81	-10.36 ± 1.99	17.05 ± 3.97
WTT^{p}	Untreated	2.34 ± 1.03	-6.86 ± 0.73	-16.60 ± 3.42	18.20 ± 3.19
WTT^{p}	Oil	5.43 ± 1.75	-7.89 ± 0.86	-11.86 ± 4.82	15.65 ± 3.79
WTT^{p}	Pigmented oil	0.61 ± 1.64	-6.50 ± 0.58	-7.39 ± 3.39	10.17 ± 2.88
WTT^{p}	Iron vitriol	-1.11 ± 1.57	-6.21 ± 1.81	-14.57 ± 4.04	15.99 ± 4.31
WTT^{p}	Silicone based	9.59 ± 3.39	-6.48 ± 1.75	-16.28 ± 4.80	20.04 ± 5.92
TW^{p}	Untreated	-2.43 ± 2.61	-5.53 ± 0.78	-15.94 ± 3.28	17.27 ± 3.23
TW^{p}	Oil	2.53 ± 1.97	-7.72 ± 0.75	-14.93 ± 4.10	17.25 ± 3.58
TW^{p}	Pigmented oil	-0.02 ± 1.17	-5.53 ± 0.46	-10.10 ± 2.88	11.64 ± 2.64
TW^{p}	Iron vitriol	-7.08 ± 1.45	-5.98 ± 0.61	-16.56 ± 2.74	19.09 ± 2.87
TW^{p}	Silicone based	6.83 ± 3.36	-2.52 ± 1.42	-9.31 ± 5.05	12.51 ± 4.68

^{s}*Spruce* ^{p}*Pine*

VTT-spruce with no surface treatment show the largest change in color (ΔE), while TW-spruce treated with pigmented oil show the smallest change in color. In Figure 1 the difference in color is shown on the actual boards. TW-spruce with silicon based surface treatment show the largest positive change in lightness (ΔL*) The silicone treatment in general has given the largest change in (ΔL*). Iron vitriol is the treatment that have had the largest darkening effect.

Figure 1a & b: Color difference between the time of painting and after nine months of exposure for VTT-spruce with no surface treatment in 1 a, and in 1 b VTT-spruce with pigmented oil.

CONCLUSIONS

The boards are still changing in color and it is still too early to determine how long time it takes for the different treatments to reach a stable color. The project continues to monitor the color change for at least another year.

ACKNOWLEDGEMENTS

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New substrates for wood modification. Characterising pore size distributions in variously dried softwood

Warren Grigsby, Elizabeth Dunningham and Hank Kroese

Scion, Rotorua 3010, New Zealand [email: warren.grigsby@scionresearch.com]

Keywords: Pore networks, Supercritical fluids, Thermoporosity, Wood pore size

EXTENDED ABSTRACT

Pore sizes within the ultrastructure of the wood cell wall are important for water movement and biological function within a tree. The pore size distribution and networks within wood generally decrease on drying wood from its green state. This has implications for further processing including preservative impregnation and wood modification treatments. Supercritical fluid (SCF) technology has been explored to dry wood Dawson *et al.* 2015, Franich *et al.* 2014). SCF has the ability to remove only unbound water delivering wood that is dried only to its fibre saturation point (FSP). SCF dewatering has advantages over traditional kiln drying in respect to dimensional stability and potentially retention of pore morphology. SCF processing creates new “dewatered” timber substrates for further processing.

In order to understand the effects of SCF dewatering on the timber, thermoporosity (Dieste *et al*. 2009, Park *et al*. 2006) employing differential scanning calorimetry (DSC) was applied to characterise the pore size distribution in wood cell walls of green *Pinus radiata* wood and whether this pore network was preserved with SCF dewatering compared to traditional kiln drying (Grigsby *et al*. 2013).

DSC thermograms employing defined heating steps (-20°C to -0.1°C) give varying melt features for each wood sample (Figure 1).

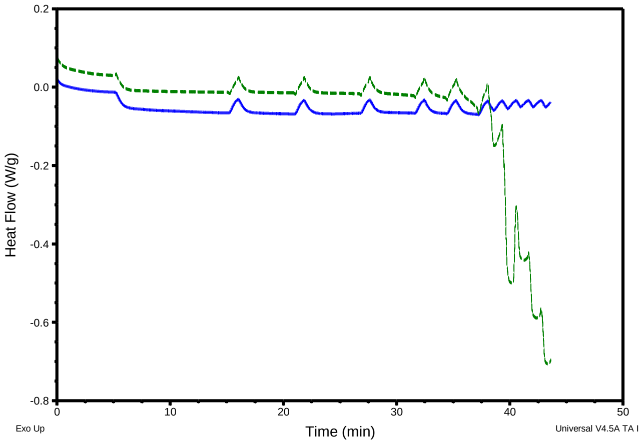

Figure 1: DSC Thermograms of green wood and dewatered early wood samples

Enthalpy changes are converted to freezing water present in defined pore sizes. This gives bound water distributions within differing pore sizes as g/g of total water. Differences in bound water evident between green and dewatered wood (at FSP, Figure 2). Analysis found the majority of bound water in green sapwood was distributed in pore sizes less than 50 nm diameter with only a small proportion present in pores sizes between 50 and 200 nm size. For dewatered wood, which is SCF processed to FSP, most bound water was found to reside in pore sizes <20 nm.

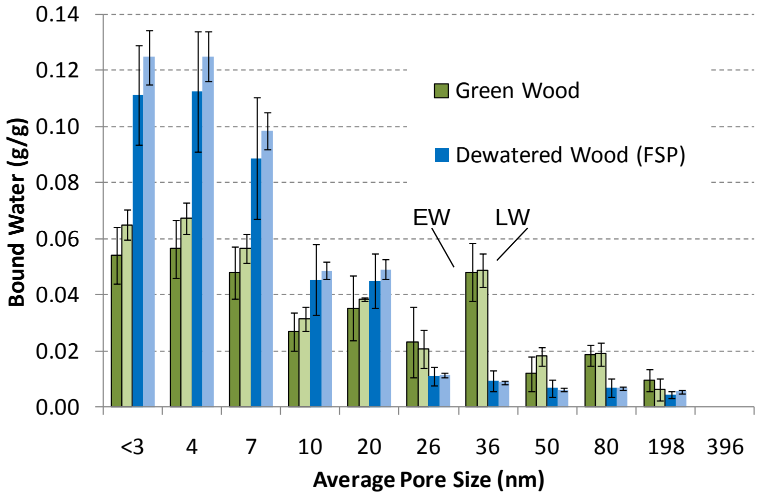

Figure 2: Pore size distributions of green and dewatered wood

When rewetted to >80% m.c., as for aqueous wood modification treatments, both dewatered and kiln-dried wood have less bound water present compared to green wood (Figure 3). This indicates a reduction in pore sizes and network accessibility for water ingress. Analysis also revealed distinctions between early wood (EW) and late wood (LW) sections where late wood sections had more water occupying smaller sized pores (<20 nm). Additionally on rewetting, there was also greater variability of pore size distributions which may infer drying does not uniformly reduce pore size volumes. Moreover, results suggest the extent of variability was generally less in the re-wetted dewatered wood sample compared to kiln-dried samples which may be attributable to SCF drying only to FSP.

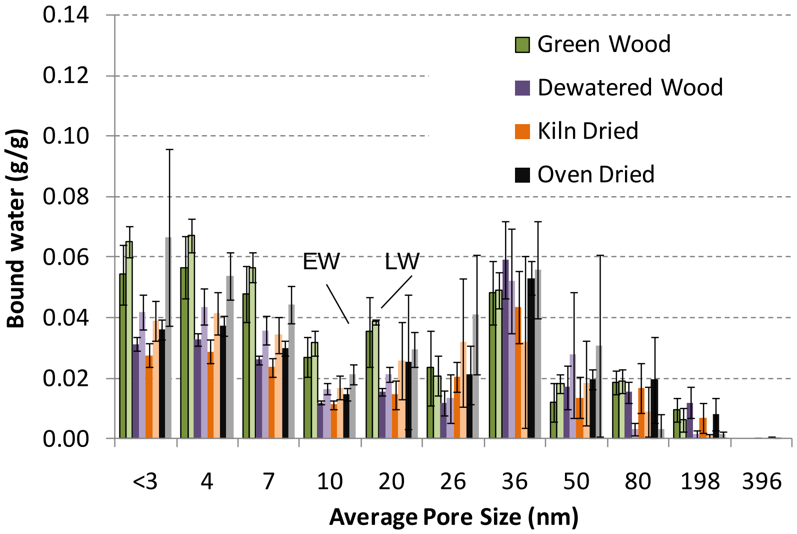

Figure 3: Pore size distributions of rewetted wood samples

Overall, application of DSC pore size analysis has revealed the distribution of pore sizes in green radiata pine with a tendency for smaller sized pores on drying. In green Pinus radiata, the bound water was distributed relatively evenly across pore sizes <50 nm dia. with a small amount of bound water in pores 50-200 nm. SCF dewatering gives greater proportion of bound water which resides in pore sizes <20 nm, consistent with wood at FSP. Dewatering or kiln drying led to proportionately less bound water on rewetting implying a reduced pore size network for water ingress. Rewetting also gives distinctions between early and late wood sections of dewatered samples and kiln and oven dried, and that variability in pore sizes >50 nm were generally less in dewatered wood than for kiln or oven drying due to only drying to FSP.

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Determination of resistance of thermally treated wood to weather conditions in different countries (HTW) - Preliminary results

Idalina Domingos[1], José Ferreira[1], Luisa Cruz-Lopes[1], Júlia Carmo[2], Jorge Martins[3], René Herrera[4], Lina Nunes [5] and Bruno Esteves[1]

[1] Center for the study of natural resources, environment and society (CERNAS)

Polytechnic Institute of Viseu, Viseu, Portugal [email: bruno@estgv.ipv.pt]

[2] Carmo Group, Lisbon, Portugal

[3] Laboratory for Process, Environmental and Energy Engineering (Lepae), Faculdade de Engenharia, Universidade do Porto, Portugal

[4] Chemical and Environmental Engineering Department, University of the Basque Country, San Sebastian, Spain

[5] National Laboratory for Civil Engineering (LNEC), Lisboa, Portugal and Centre for Ecology, Evolution and Environmental Changes (CE3C), Azorean Biodiversity Group, University of the Azores, Angra do Heroísmo, Portugal

Keywords: accelerated weathering, heat treatment, surface analysis, weathering

ABSTRACT

Pine samples were treated in an industrial facility (Palser, Lda) at 212 ºC in accordance to Thermo D class from Thermowood ®. Before the exposure, several properties of untreated and heat treated maritime pine wood (*Pinus pinaster*, Ait) were determined. Surface analysis included the determination of colour, roughness and gloss. Untreated and heat treated wood were positioned in treated wood racks at 45 degrees inclination and southern exposure in two exposure sites in Portugal and Spain. Samples will be removed for evaluation yearly until the end of the planned exposure time of five years. In parallel accelerated weathering will be done using a QUV machine. Simulated processes corresponded to exposure from six month (75 h) to five years (750 h) in order to compare it with the natural weathering. Preliminary results from accelerated -weathering and field exposure (Viseu-Portugal) are presented here.

INTRODUCTION

Heat treatment is by now a well-known modification procedure to increase wood stability and durability has reported before (Esteves & Pereira, 2009). One of the most successful commercial processes is the Thermowood process that started in Finland but is now used in several countries like Sweden, Turkey, Japan and Portugal. The treatment is done with steam, with less than 3 to 5% oxygen without pressure and with a minimum speed of 10 m/s. The process begins with a rapid increase in temperature of the oven with heat and steam up to 100° C, followed by a gradual increase up to 130° C to near zero humidity. Then, heat treatment is made between 185° C to 230° C for 2 to 3 hours. Finally, the temperature decreases to 80-90° C.

Deterioration by abiotic agents like solar radiation, rain, snow and sleet, wind and humidity changes is generally linked to weather exposure conditions. Solar radiation affects the wood due to UV radiation that causes photochemical damage in lignin and extractives. The UV degradation process is driven by the formation of free radicals that are formed by oxidation of phenolic hydroxides. Mechanical damage on the surfaces, is particularly a result of retraction and swelling of the wood. With the leaching of soluble compounds, the most photo-resistant compounds are exposed in the surface leading to their degradation. With time, the wood acquires a greyish tone, due to the residual cellulose and fungal growth like that of *Aureobasidium pullulans*. One of the main difficulties to estimate wood service life in Europe is the variability of climates between regions particularly the average number of sunshine hours per year. Cities like Lisbon, Madrid or Athens show an average well above 2500 hours of sunshine per year far superior to the values measured on Northern European countries which are typically bellow 1800 hours per year. The expected level of degradation by UV radiation is thus significantly higher in Southern Europe though most wood modification developments were initially targeted to Nordic countries.

This work was done in the framework of the project PROJ/CI&DETS/2016/0010-Determination of resistance of thermally treated wood to weather conditions in different countries (HTW). The goal of this project is to study the degradation of thermally modified wood by Thermowood process in countries where solar radiation is higher like Portugal and Spain and compare it to accelerated weathering. A secondary goal is to obtain enhanced service life data to be used in LCA calculations in these countries.

EXPERIMENTAL

Pine samples (*Pinus pinaster*, Ait) were treated in an industrial facility (Palser, Lda) at 212 ºC in accordance to Thermo D class from Thermowood ®. Untreated and heat treated wood were positioned in treated wood racks at 45 degrees inclination and southern exposure in two exposure sites in Portugal (Viseu) and Spain (San Sebastian). Samples will be removed for evaluation yearly until the end of the planned exposure time of five years. Similar samples were positioned in a QUV machine from 75 h to 750 h. The field test exposure started in Portugal (Viseu) in February 2018 and in Spain in October 2017. Therefore, the natural weathering has not yet completed the first year of exposure and only preliminary visual comparison between natural (Viseu exposure site) and artificial weathering was done.

Several properties of untreated and heat treated pine wood were determined. Surface analysis included the determination of colour, roughness and gloss. Colour was measured by the CIELAB method determining the colour parameters L*, a* and b* for untreated and treated wood, before exposure and after being exposed to accelerated weathering. Glossiness was determined at 20º, 60º and 85º with a gloss meter. Roughness was measured in a Surftest SJ-400 from Mitotoyo. Average roughness (Ra) and the average distance between the highest peak and lowest valley in each sampling length (Rz) were determined.

RESULTS AND DISCUSSION

The appearance of natural and artificially weathered wood after 16 weeks and from 75 to 7500 hours of QUV are shown in Figure 1. Although the natural weathering exposure has not yet completed 6 month all the samples already exhibit a clear greyish tone. Visually there is no significant difference between untreated and heat treated wood with just a little darker tone for treated wood.

In artificial weathering the differences between untreated and heat treated wood are much more pronounced. The colour of untreated wood has turned from light to dark brown with some greying for higher aging periods. Aged heat treated wood has a lighter brown than the original colour, nevertheless the differences between unaged and aged samples are much smaller than with natural weathering. These preliminary results show that the assumption that 75 h in the QUV would simulate 6 month in the exterior is far from true regarding the surface colour. Even after 750 h of aging the surface colour of artificial aged wood has still a darker brown than the 6 month old natural weathered wood.

Figure 1: Visual appearance of natural (left) and artificially (right) weathered wood

Figure 2 presents the colour variation along the aging process for untreated and heat treated wood. Results show that for untreated wood lightness (L*) decreases in the first 150 h of aging from 76 to about 60, staying approximately constant afterwards. The parameter a* increase in the beginning decreasing later on while b* follows a similar pattern but with much smaller variations. In heat treated wood the initial lightness (37) is approximately constant along the aging process with small variations, the same happening for a* and b* parameters.

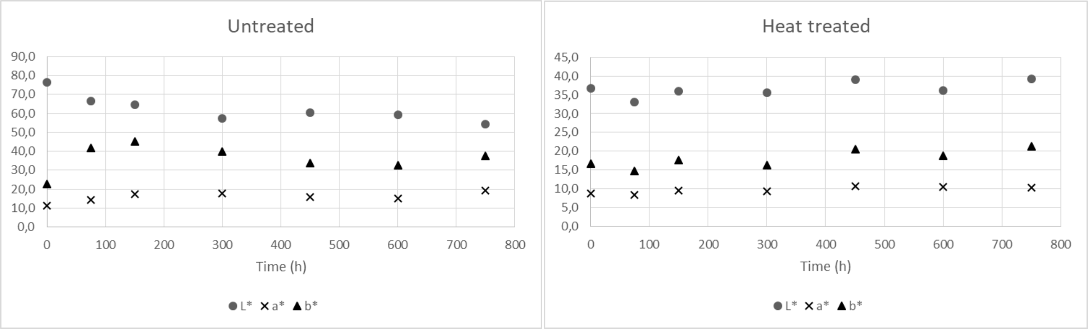

Figure 2: Colour variation along the aging process for untreated (left) and heat treated wood (right)

Figure 3 presents the roughness variation along the aging process for untreated and heat treated wood. Results show that for untreated wood both Ra and Rz increase in the beginning until about 300 h of explosion being approximately constant after that, similarly to heat treated wood although the increase in roughness is higher for untreated wood.

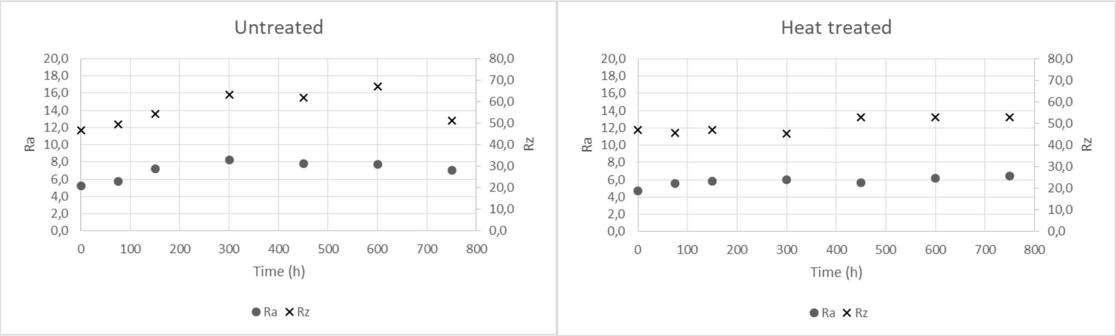

Figure 3: Roughness variation along the aging process for untreated (left) and heat treated wood (right)

Table 1 presents the glossiness variation along the aging process for untreated and heat treated wood. Results show that for untreated wood glossiness decreases slightly with the aging process. This decrease is essentially seen on 20º and 65º angles, nevertheless the correct angle for glossiness determination should be 85º due to the matt surface presented by the untreated and heat treated samples with glossiness lower than 30 GU. Heat treated wood shows a very erratic behaviour, especially at 85º angle since no clear decrease or increase could be found. This can be due to surface irregularities that usually decreases the measured value of gloss, especially at higher angles as stated before by Bekhta et al. (2014).

Table 1: Glossiness variation along the aging process for untreated and heat treated wood

	Untreated				**Heat treated**		
Time (h)	**20º**	**60º**	**85º**	**Time (h)**	**20º**	**60º**	**85º**
0	1,0	2,6	1,4	0	0,3	1,5	3,2
75	0,8	2,5	1,3	75	0,3	1,5	2,9
150	0,7	2,4	1,3	150	0,3	1,6	2,4
300	0,6	1,7	1,1	300	0,3	1,7	3,1
450	0,6	1,9	1,2	450	0,3	2,0	2,7
600	0,6	1,7	1,0	600	0,3	1,5	1,8
750	0,5	1,6	1,4	750	0,3	1,7	2,7

CONCLUSIONS

Preliminary results show that, for maritime pine, the assumption that 75 h in the QUV would simulate 6 month in the exterior is far from true regarding the surface colour. With artificial weathering lightness (L*) decreases staying approximately constant afterwards for untreated wood while no significant changes were observed for heat treated wood. Roughness increase in the beginning until about 300 h for untreated wood being approximately constant after that, similarly to heat treated wood although with a higher increase. Untreated wood glossiness decreases slightly with the aging process but no clear increase or decrease could be found for heat treated wood.

ACKNOWLEDGEMENTS

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Investigation of *Abies alba* wood thermal stability according to its radial position

Joël Hamada[1], Anélie Pétrissans[1], Julien Ruelle[2], Frédéric Mothe[2],
Francis Colin[2], Mathieu Pétrissans[1], Philippe Gérardin[1]

[1] Université de Lorraine, Inra, EA 4370 USC 1445 LERMAB, Faculté des Sciences et Technologies,
BP 70239, 54506 Vandoeuvre-lès-Nancy Cedex, France [email : philippe.gerardin@univ-lorraine.fr]
[2] Université de Lorraine, AgroParisTech, Inra, UMR 1434 SILVA, Centre Inra Grand-Est Nancy,
Route d'Amance, 54280 Champenoux, France [email : frederic.mothe@inra.fr]

Keywords: earlywood, heartwood, juvenile wood, latewood, sapwood, silver fir, thermal degradation, variability

ABSTRACT

Most of the defects affecting heat treated wood quality are often attributed to heterogeneous heat transfers in industrial kilns. Even if interspecific variability of wood has been reported to affect thermal degradation of the material, little has been reported on the effects of intraspecific variability. The aim of this work was to study the effect of intraspecific variability of silver fir (*Abies alba* Mill.) wood on its thermal stability.

For this purpose, wood samples were sampled along the radius of cross-sections to estimate the effect of radial position on wood thermal degradation. Sampling was carried out on discs of 4 trees, 2 resulting from dynamic growth stand and 2 from standard growth stand. Study was performed at different scales: at wood compartments scale involving juvenile and mature heartwood, transition zone between heartwood and sapwood and sapwood as well as at intra-ring scale. Wood samples were ground to sawdust and subjected to thermo-gravimetric analysis and chemical analysis. Juvenile heartwood was shown to be more sensitive to thermal degradation than other compartments. The thermal behaviour of sapwood was not particularly different from that of heartwood, and the presence of extractives did not influence significantly thermal degradation. Fast growing wood characterized by larger annual rings with high earlywood/latewood ratio resulting from tinning was shown to present quite similar behaviour than juvenile heartwood with higher susceptibility to thermal degradation. Taking into account the high proportion of cellulose contained in the S2 layer of secondary wall, it can be assumed that cellulose content of wood compartments with high earlywood content will result in slightly lower cellulose content comparatively to wood compartments with higher latewood content. Consequently, compartments with lower cellulose content could be more susceptible to thermal degradation due to higher thermal suceptibility of hemicelluloses and lignin. Thermo gravimetric analysis was also performed for earlywood (EW) and latewood (LW) sampled in the different annual rings for the four tested trees. Earlywood was more sensitive to thermal degradation than latewood explaining the higher susceptibility of fast growing heartwood containing larger rings with higher contents of earlywood. These results are consistent with those previously found with *Quercus robur* L. wood and *Quercus petraea* L. wood suggesting that, independently of the wood species, earlywood was more susceptible to thermal degradation than latewood.

INTRODUCTION

A lot of studies have been carried out to understand the effect of heat treatment on modification of wood cell wall polymers and the effect of these modifications on wood properties (Esteves and Pereira 2009, Gérardin 2016). More recently, studies focused on the development of quality control methods to assess the quality of thermally modified products at industrial scale (Candelier *et al.* 2016). It is often postulated that heterogeneity of heat transfer in the wood pile in the industrial kiln may be one of the main factor explaining the heterogeneity of heat treated products. Wood is naturally variable and important variations of wood properties can be found inter-specifically, intra-specifically and even within a same tree (Bao *et al*. 2001; Kimberley *et al*. 2015; Murphy and Cown 2015). Silver fir wood properties have been reported to vary according to wood radial position (González-Rodrigo *et al*. 2013; Bertaud and Holmbom 2004). Wood variability may be the results of numerous factors like genetics, climate, landform, soil quality, up to human actions like forest management policies. Forest management influences directly growth of the trees impacting their diameter and height as well as wood quality (Bruchwald *et al.* 2015). Numerous studies reported the effect of forestry on wood density or chemical composition for both hardwoods and softwoods species (Karlsson *et al*. 2013). Contrary to the effect of interspecific variability of wood on wood thermal degradation (Candelier *et al*. 2011), the effect of intraspecific variability has been relatively little studied. The aim of this study is to investigate the effect of intraspecific variability of Silver fir wood (*Abies alba* Mill.) on its thermal degradation. For this purpose, thermal stability of juvenile heartwood, mature heartwood, sapwood, earlywood and latewood samples taken along the radii of the cross section of four Silver fir trees resulting from two different forest management was investigated using thermo gravimetric analysis under conditions similar to that used during wood thermal modifications.

MATERIAL AND METHODS

Materials

Four silver fir (*Abies alba* Mill.) trees from an experimental forest of the French State Forestry Administration (ONF) in the Eastern France where used in this study. The forest is located in the Jura Mountains at 900 m altitude. As described by the ONF, four forestry schedules were implemented in this forest in winter 1990/1991, where silver fir was mixed with other species, mainly spruce (*Picea* Mill.) and European beech (*Fagus sylvatica*). Two schedules (stands) were selected for the present study. The first one corresponds to control stand without thinning referred to as “control modality”, the second one corresponds to dynamic stand with thinning schedules referred to as “strong modality”. For each stand, 2 trees were selected (trees 1 and 2 for dynamic, trees 3 and 4 for control). In dynamic stand, wide growth rings formed after the post-thinning period could be easily observed on the cross-section, whereas any specific growth rings feature could be noticed on control trees cross-section. The age of trees 1, 2, 3 and 4 was estimated from stump discs to 80, 50, 51 and 55 years, respectively. However, the number of annual rings counted at breast height was significantly lower with values of 49, 35, 29 and 44 rings of trees 1, 2, 3 and 4, respectively due to the very slow initial growth of silver fir.

Intraspecific radial variability measured by X-ray micro-densitometry

One 30 mm thick disc was sampled from each tree of both dynamic and control modalities at breast height (1.3 m) (total of 4 discs) for the determination of the radial variation of ring width and wood density. The growth variation was characterized by X-ray micro-densitometry using a micro-focus X-ray source (Hamamatsu L9181-02 130 kV) and a digital X-ray detector (Varian PaxScan 4030R). The radial profiles of growth rings and wood density were computed using the Cerd software suite (Mothe et al. 1998).

Thermo gravimetric analysis

Radii from the four trees were taken as shown on figure 1 from cross section taken at breast height (1.3 m aboveground).

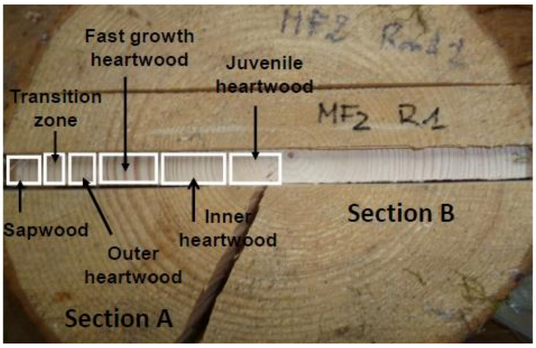

Figure 1: Sampling procedure for analysis of wood's compartments thermal stability

The section A was divided into juvenile heartwood, mature heartwood and sapwood. Mature heartwood was then separated into inner mature heartwood (IHW), fast growing heartwood (FGHW) in the case where the trees grown under dynamic forest management, outer mature heartwood (OHW) and transition zone (TZ). Growth rings were taken from the section B for only juvenile and mature heartwood and separated into earlywood (EW) and latewood (LW), when ring width was large enough for sampling. All the samples were then ground and sieved to obtain particles size < 0.160 mm for thermos gravimetric analysis (TGA) and between 0.200 mm and 0.400 mm for chemical analysis. Thermo gravimetric analysis (TGA) was performed under nitrogen on 10 mg samples using a Mettler ToledoTGA/DSC STARe system. The heat treatment schedule included a first step of drying at 103°C four 30 mn followed by a second step of thermal treatment at 230°C for 2 h. The heating rate and gas flow were 10 K.mn^{-1} and 50 mL.mn^{-1}, respectively. Three analyses were performed on wood samples issued from section A (juvenile heartwood, mature heartwood and sapwood), while only one experiment was performed for each sample of earlywood and latewood sampled in section B. The mass loss (ML) due to thermal degradation was calculated according to the following formula:
$ML\ \% = 100 \times (m_0 – m_1)/m_0$
Where m_0 is the initial dry mass of the sample at 103°C before thermal treatment at 230°C and m_1 the final sample mass after cooling at 100°C.

RESULTS AND DISCUSSION

Radial variation of growth rings width and density is presented in figure 2. Wood ring density and growth ring width present opposite behaviours. Generally, ring width increases when ring wood density decreases. This is particularly obvious for dynamic stand samples, where ring width increased considerably after thinning. Average ring wood density is all cases higher for juvenile heartwood compared to mature heartwood. In all cases, latewood presents as expected higher density than earlywood in connection the thickness of latewood tracheids. Juvenile wood presents generally larger rings compared to classical mature wood. Same remarks can be drawn for trees 1 and 2 grown under dynamic stand conditions for which, the rings produced just after thinning present larger width. Ring density of fast growth rings produced after thinning decreased from values comprised between 950 and 1000 kg.m^{-3} to values comprised between 800 and 700 kg.m^{-3} due to the higher proportion of earlywood formed during favourable growth conditions (Cameron *et al*. 2005).

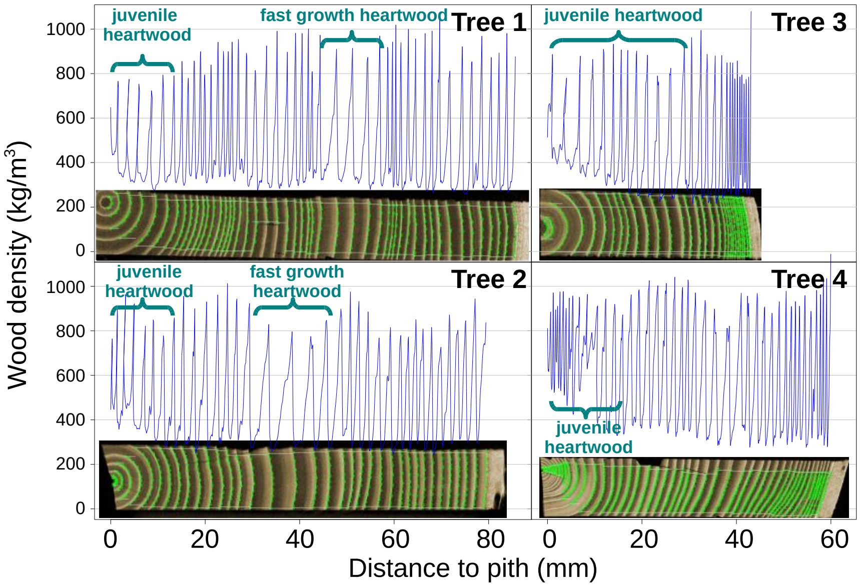

Figure 2: Radial density profile (blue) and X-ray images with ring limits (green)

The thermal stability of the different wood compartments of silver fir wood sampled along the radius of the cross-section is presented in figure 3.

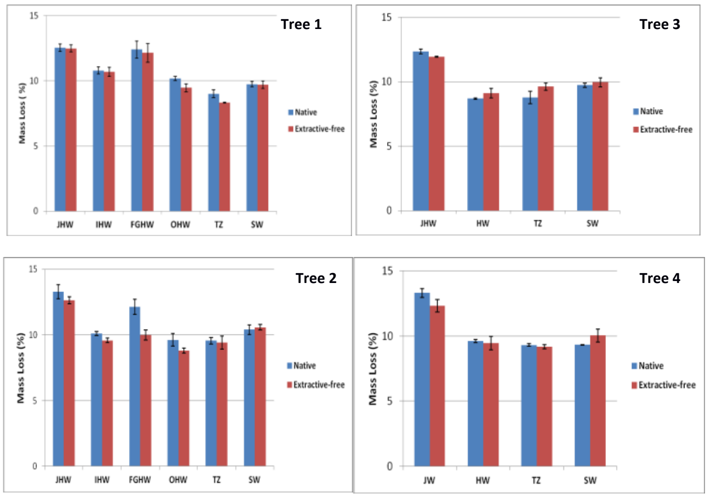

Figure 3: Thermal stability of the different wood compartments treated at 230°C for 2 hours of the different trees grown under dynamic stand (trees 1 and 2) or control stand conditions (trees 3 and 4). First bar corresponds to native sample, second bar to extractive free sample

For all studied trees, the juvenile heartwood was more susceptible to thermal degradation than the other wood compartments. No significant differences were observed between the different compartments of heartwood excepted for fast growing heartwood resulting from dynamic stand, which is more sensitive to thermal degradation for the both trees studied. Sapwood presents quite similar thermal behavior than transition zone and outer or inner heartwood independently of the forest management used. Properties of juvenile heartwood are usually related to shorter cell length, higher micro-fibril angle, lower density due to higher proportions of earlywood formed (Cameron *et al.*, 2005). In conifers, lower cellulose content, thinner cell wall, lower percentage of latewood, higher lignin content, and more compression wood, determine the characteristics of juvenile heartwood. These characteristics are also largely attributed to earlywood being formed in favorable growth conditions. As juvenile heartwood and fast growing heartwood contain high proportions of earlywood formed as a result of thinning, this higher proportion of earlywood comparatively to latewood found in fast growing heartwood seems at the origin of its higher thermal susceptibility. Indeed, earlywood is characterized by tracheids with thinner cell walls and larger diameter lumina. Taking into account the high proportion of cellulose contained in the S2 layer of secondary wall, it can be assumed that cellulose content of wood compartements with high earlywood content will result in slightly lower cellulose content comparatively to wood compartments with higher latewood content. Consequently, compartments with lower cellulose content could be more susceptible to thermal degradation due to higher thermal susceptibility of hemicelluloses and lignin. Figure 4 presents mass losses recorded using thermo gravimetric analysis for earlywood (EW) and latewood (LW) sampled in the different annual rings for the four tested trees.

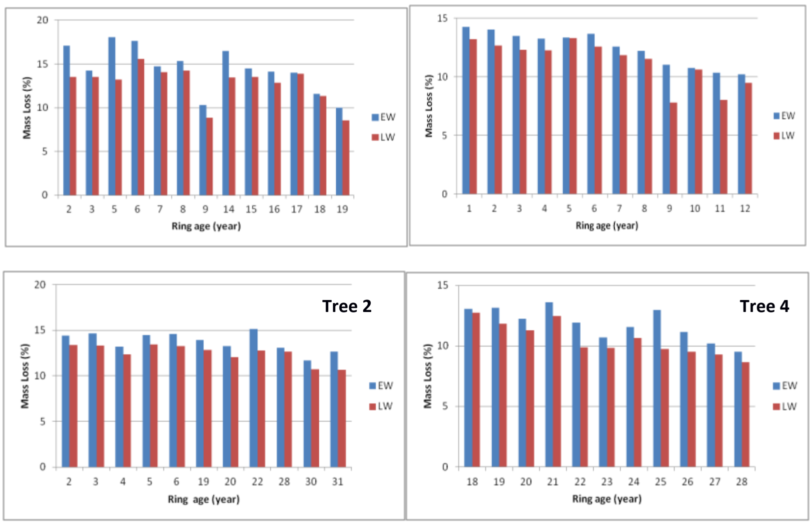

Figure 4: Thermal stability of earlywood (EW) and latewood (LW) samples treated at 230°C for 2 hours of the different trees grown under dynamic stand (trees 1 and 2) or control stand (trees 3 and 4) First bar corresponds to earlywood, second bar to latewood

EW was more sensitive to heat than LW whatever the tree or silviculture schedule. These results are consistent with those previously found with *Quercus robur* L. wood (Shchupakivskyy *et al*. 2014) and *Quercus petraea* L. wood (Hamada *et al*. 2017) suggesting that earlywood was more susceptible to thermal degradation than latewood independently of the wood species. Forest management involving production of Silver fir wood with larger annual rings and higher quantities of earlywood appears therefore as a factor influencing thermal stability of wood and consequently its thermal degradation during thermal modification processes. Boards containing different amounts of earlywood may therefore present different behaviour to thermal degradation explaining a part of the variability recorded during numerous thermo-modification processes.

CONCLUSIONS

The aim of this study was to investigate the effect of Silver fir wood intraspecific variability on its thermal stability. Thermogravimetric analyses indicated that radial position influenced directly thermal behaviour of wood sample to thermal degradation. Juvenile heartwood and fast growing heartwood present higher susceptibility to thermal degradation comparatively to other wood compartments. Chemical and anatomical features can be regarded as the main reasons for the higher thermal reactivity of both juvenile and fast growing heartwood. Dynamic forest management can consequently impact thermal reactivity of wood due to the increase of earlywood production after thinning operations. Wood quality and or variability are consequently, as for other many wood uses, important parameters to produce homogeneous heat treated materials.

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Properties improvement of bamboo materials through furfurylation

Li Wanju[1,2,3], Wang Hankun[1,2], Liu Minghui[1,2], Yu Yan[1,2]

[1] Department of Biomaterials, International Center for Bamboo and Rattan, Beijing, China
[2] SFA and Beijing Co-built Key Lab for Bamboo and Rattan Science & Technology
[3] Guangdong Provincial Key Laboratory of Silviculture, Protection and Utilization, Guangdong Academy of Forestry, Guangzhou, China

Keywords: Bamboo, furfurylation, physical-mechanical properties, durability, nanoindentation.

ABSTRACT

Bamboo is much harder to be chemically treated than wood because the former is characterized with much poorer transverse permeability than the later. Furfurylation is recognized as an efficient strategy for wood modification. In this study, bamboo strips were modified with furfuryl alcohol (FA) catalysed by a new composite acidic catalyst through a common vacuum and pressure process. The effect of FA concentration (15%, 30%, 50%, and 70%), curing temperature (95℃, 105℃, 115℃, 125℃) and curing time (1.5 h, 3 h, 5 h, 8 h) on the properties of modified bamboo were systematically investigated. The weight percent gain (WPG), equilibrium moisture content (EMC), anti-swelling efficiency (ASE), mechanical properties such as modulus of rupture (MOR), modulus of elasticity (MOE) and parallel-to-grain compressive strength (CS) and various biological resistances were all evaluated.

The results show that FA concentration is the most important parameter for bamboo furfurylation, while curing temperature and time play much less role for the defined range in this study. After furfurylation, the color of bamboo is changed to brown, and nearly all the properties of bamboo can be improved by furfurylation with different extent. The EMC of bamboo reduces significantly by around 40 to 50% after furfurylation. Furfurylation of bamboo appears to resistance to mould and decay fungi. 10% WPG treated bamboo shown 100% anti-mold efficiency and belonged a very durable level resistance to decay fungi. 6%~10% and 11%~20% WPG furfurylated bamboo belonged to “I” and “0” class termite resistance, respectively. Additionally, the mechanical properties of furfurylated bamboo are slightly improved. However, the dimensional stability of bamboo are negatively affected by furfurylation, which is unexpected and demonstrated to be mainly correlated to the excessive drying induced collapse of parenchymal cells in bamboo after furfurylation.

INTRODUCTION

Bamboo is an important lignocellulose-based natural resource, and bamboo is popular as feedstock of paper, decorative material in furniture surfaces, wallboards, fencing and flooring due to its unique grain and good abrasion resistance, (Cheng et al., 2013； Liese and Köhl, 2015). However, the application of bamboo and bamboo products is limited because of a low natural durability of bamboo due to its large amount of starch, sugar, protein and other salt substances (Wei et al. 2013).

In the past 20 years, furfurylation has become a new and effective method for modifying the properties of wood, to produce significant improvements in physical-mechanical performance and durability (Gobakken and Westin 2008; Hadi et al. 2005). Whereas studies on furfurylation of bamboo are meagre (Li et al., 2014). Furfuryl alcohol is an organic chemical with strong-polarity and low-molecular weight. During furfurylation, polymers form in the cavities and cell walls under elevated temperatures, as long as grafting occurs between FA or poly-FA and wood cell-wall polymers (Nordstierna et al. 2008; Lande et al. 2008). Therefore, this method might be suitable for bamboo due to its anatomical structure-vascular bundles embedded in parenchymatous ground tissue without radial tissues, like the rays found in wood (Sánchez et al. 2013).

The purpose of this study is to evaluate the suitability of furfurylation for bamboo strips. Furthermore, to evaluate the influence of furfurylation with different process on the physical-mechanical properties and the durability resistance to mould, decay fungi and termite of bamboo.

EXPERIMENTAL

Bamboo furfurylation

Moso bamboo specimens was placed in a custom-built reactor (PF-2) and treated in vacuum for 30 min followed by 0.5 MPa of pressure for 3 h, then immersion in FA solutions for 36 h at normal pressure. Then the bamboo specimens were cured at different curing temperature and time respectively. After polymerization, the treated samples were further dried until an oven dried state was achieved.

Physical and mechanical properties test

Physical properties

The Weight percentage gain (WPG) was calculated according to (Eqn.1).

$$\text{WPG}\ (\%) = ((M_1 - M_0)/M_0) \times 100 \qquad (1)$$

Where M_1 and M_0 is the oven-dry mass of the before and after furfurylated bamboo samples, respectively.

The Equilibrium moisture content (EMC) was calculated.

$$\text{EMC}\ (\%) = ((M_2 - M_1)/M_1) \times 100 \qquad (2)$$

Where M_2 and M_1 is the conditioned and oven-dry mass of the furfurylated bamboo samples, respectively.

The dimensional stability of bamboo was characterized by anti-swelling efficiency (ASE). The coefficient of wet expansion (α) and ASE were calculated as Eqn. (3) and (4), respectively.

$$\alpha\ (\%) = ((V_{wet} - V_{dry})/V_{dry}) \times 100 \qquad (3)$$

$$\text{ASE}\ (\%) = ((\alpha_0 - \alpha_1)/\alpha_0) \times 100 \qquad (4)$$

Where α_0 and α_1 represent the coefficient of wet expansion of the untreated and furfurylated bamboo samples.

Mechanical properties

Modulus of rupture (MOR) and Modulus of elasticity (MOE) of bamboo were measured at three-point bending model. The diameter of the loading head was 30 mm, with a bearing span of 120 mm. The loading speed was set at 2 mm/min for bending tests. Parallel-to-grain compressive strength (CS) of bamboo was tested according to the Chinese national standard GB/T 15780-1995, and the maximum compressive load the sample stood for more than 90 s without collapse, was recorded.

Durability of furfurylated bamboo

Laboratory testing of resistance to moulds

Resistance to mold was evaluated following the method described in the Chinese National Standard (GB/T 18261-2000) and four moulds were used.

Laboratory testing of resistance to fungi

Resistance to decay was evaluated by following a method derived from GB/T 13942.1-2009. The weight loss ratio (WLR) was calculated as Eqn. (5) and used to assessed the decay resistance of sample.

$$\text{WLR}\ (\%) = ((M_3 - M_4)/M_3) \times 100 \qquad (5)$$

Where WLR is the weight loss ratio and M_3 and M_4 is the weight of the samples before and after test, respectively.

RESULTS AND DISCUSSIONS

The physical properties of bamboo

Table 1 shows the WPG is closely related to the concentration and molecular weight of the modifier agent, and the WPG of furfurylated bamboo increased from 11.2% to 32.5%, with the increase of the concentration from 15% to 70%. Furthremore, the WPG of treated bamboo is 11.2% with only 15% concentration of FA, which indicates that FA solution easy to impregnate into bamboo and cured well.

Table 1: The physical properties of untreated and furfurylated bamboo

NO	FA Concentration [%]	Curing time [h]	Curing temperature [℃]	WPG [%]	EMC [%]	ASE(V) [%]
1	15	3	105	11.2±2.0	6.9±1.1	-77.9
2	30	3	105	18.9±2.3	5.2±0.3	-144.2
3	50	3	105	22.8±2.4	4.8±0.7	-70.5
4	70	3	105	32.5±6.1	5.7±0.7	3.6
5	15	3	95	9.7±1.5	6.6±0.3	-108.4
6	15	3	105	10.0±2.0	6.3±0.2	-64.2
7	15	3	115	11.3±1.1	6.2±0.4	-138.9
8	15	3	125	10.8±1.1	6.3±0.2	-96.8
9	15	1.5	105	6.4±1.1	6.6±0.5	-180
10	15	3	105	10.0±2.0	6.3±0.2	-64.2
11	15	5	105	9.9±1.8	4.5±0.2	-56.8
12	15	8	105	7.5±2.0	5.3±0.2	-76.8
0	0	0	0	0	10.5±0.4	--

Table 1 presents the EMC values of the bamboo specimens, the EMC of furfurylated bamboo exhibited a significant reduction compared to the untreated bamboo. The lowest EMC values (4.2%) occurred for furfurylated with 15% FA concentration at 105 ℃ for 3 h, corresponding to 60% change in relation to untreated bamboo. Furfurylation reduces the EMC of bamboo by the blocking effect of FA resin inside the bamboo cavity and even the cross-linkage with the bamboo cell components. In this study, the ASE of furfurylated bamboo as show in Table 1 is negative value, the dimensional stability of furfurylated bamboo is worse than that of untreated bamboo. With farther analysis we found that the size of furfurylated bamboo changed greatly due to the special structure of bamboo.

The mechanical properties of bamboo

Figure 1(a) presents the mechanical properties results of the untreated bamboo and furfuylated bamboo with different FA concentration. The mechanical properties of furfurylated bamboo increased firstly and then decreased with the FA concentration increased from 15% to 70%. The improved mechanical properties were observed when FA concentration was 15%, which MOR, MOE and CS of furfurylated bamboo was 108 MPa, 8.36 GPa and 43.5 MPa, respectively, corresponding to 25%, 12% and 17% increase in relation to untreated bamboo. Figure 1(b) depicts the mechanical properties change with the curing temperature increased from 95℃ to 125℃. The figure showed that MOR and CS of furfurylated bamboo were higher than untreated bamboo, while the MOE improved less. Figure 1(c) depicts the macroscopic mechanical properties of furfurylated bamboo was improved within small extent as the curing time last from 1.5 h to 8 h. Overall, 3 h might be enough for furfurylated bamboo with 15% FA concentration cured at 105℃. In general, furfurylation can improved the mechanical properties of bamboo within limits.

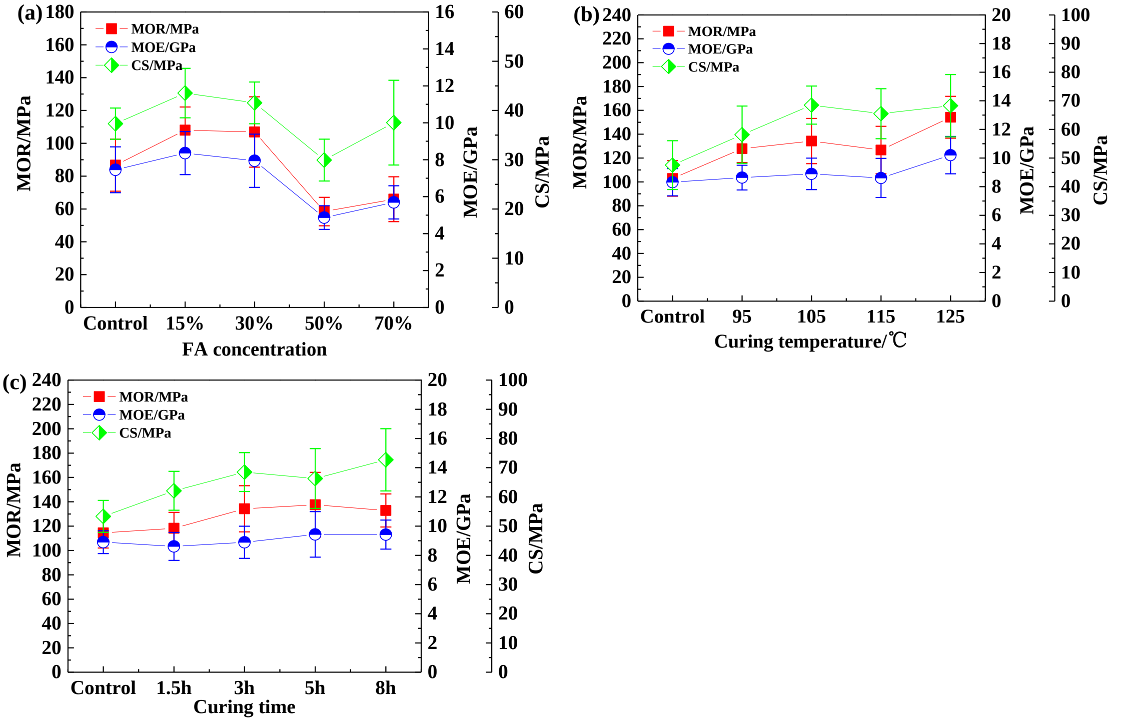

Figure 1: The MOR、MOE and CS of treated bamboo with different FA concentration (a), curing temperature (b) and curing time (c)

The durability of furfurylated bamboo

Laboratory tests with mould fungi

In this study, the furfurylated bamboo samples treated with different FA concentration were uesed in the laboratory tests. After one month's infection by *A. niger*, *P. citrinum*, *T. viride* and *B. theobromae*, the untreated bamboo samples showed little resistance to mould (Table 2). In contrast, there was no mycelium appeared on the surface and end surface of other samples infection of the four fungi. Furfurylation can improve the mould resistance properties of bamboo, which is attributable to the entering channel of mould into bamboo was blocked and the nutrient substance in the cavities of bamboo were removed. Additionally, other possible reason is that the moisture content of furfurylated bamboo decreased significantly and the pH value changed, which leading to the surrounding of bamboo surface were no longer suitable for mould growth.

Table 2: Overall appraisal of the fungicides against the test fungi with different FA concentration

Samples	**FA concentration [%]**	**WPG [%]**	**Types of mould**				**Resist effectiveness [%]**
			A. niger	***P. citrinum***	***T. viride***	***B. theobromae***	
Control	0	0	4	4	4	4	0
Furfurylated bamboo	15	10	0	0	0	0	100
	30	18.9	0	0	0	0	100
	50	22.8	0	0	0	0	100
	70	32.5	0	0	0	0	100

Laboratory tests with decay fungi

There is a significant effect of furfurylation on the susceptibility of the bamboo samples (Table 3). The average weight loss values of untreated bamboo blocks by white- and brown-rot fungus was 60.48% and 54.36%, respectively. In contrast, the WLR of the furfurylated bamboo was only 4.37~9.83%. Table 3 shows the furfurylated bamboo with high FA concentration had higher WLR, a possible reason for this result that furfurylated bamboo with higher FA concentration might not fully cured and run off during the test, leading to the WLR was higher.

Table 3: The weight loss ratio of furfurylated bamboo with different FA concentration

Samples	**FA concentration [%]**	**WPG [%]**	**WLR [%]**	
			Trametes versicolor	***Gloeophyllum trabeum***
Control	0	0	60.48	54.36
Furfurylated bamboo	15	10	7.29	7.89
	30	18.9	6.85	4.37
	50	22.8	8.95	9.12
	70	32.5	9.83	8.98

CONCLUSION

This study has investigated that furfurylatuon is suitable for bamboo modification. The results show nearly all the properties of bamboo can be improved by furfurylation with different extent. The EMC of bamboo reduces significantly by around 40 to 50% after furfurylation. Furfurylation of bamboo appears to resistance to mould, decay fungi and termite attack. 10% WPG treated bamboo shown 100% anti-mold efficiency and belonged a very durable level resistance to decay fungi. Additionally, the mechanical properties of furfurylated bamboo are slightly improved. However, the dimensional stability of bamboo (both in tangential and radial direction) are negatively affected by furfurylation except the longitudinal direction, which is unexpected and demonstrated to be mainly correlated to the excessive drying induced collapse of parenchymal cells in bamboo after furfurylation.

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Veneer modification with fire retardant chemicals

Saara Hautamäki[1], Michael Altgen[1], Tuomas Hänninen[1] and Lauri Rautkari[1]

[1]Department of Bioproducts and Biosystems, School of Chemical Engineering, Aalto University, P.O. Box 16300, FI-00076 Aalto [email: saara.hautamaki@aalto.fi]

Keywords: Adhesion, Fire retardant chemicals, Veneer modification, Wood combustion

ABSTRACT

The progress in the development of new fire retardant chemicals is relatively slow, especially in the field of wood technology, and the most common chemicals already have a long history of use. They include those based on silica, boron and boric acid, inorganic salts of phosphorous and nitrogen and their synergistic combinations. Even though the components of most fire retardant chemicals available on the market have been known for a long time, only limited information is available on their effects on adhesion and other veneer properties. In this work, veneer modification with sodium silicate (SS, also known as water glass) and diammonium phosphate (DAP) was investigated. The focus was especially on the thermal behaviour and adhesion properties of the modified veneers. Thermal properties and combustibility were investigated with thermogravimetric analysis (TGA) and a simple fire resistance test, where the samples were ignited and the mass loss and the duration of flaming and glowing combustion was recorded. Wettability and glue bond strength of the modified veneers was analysed by contact angle measurements using the sessile drop method, and by automated bonding evaluation system (ABES) using a phenol-formaldehyde resin. With TGA, it was found that both sodium silicate and DAP had an effect on how the thermal degradation of the modified samples proceeded. This was confirmed in the actual fire resistance test, where a clear reduction in the mass loss of the samples was observed. However, this did not translate to clear changes in the flaming or glowing combustion times of the samples. In fact, the sodium silicate treatment actually prolonged the glowing combustion time. Curiously, a notable increase in the glue bond strength of DAP modified veneer material was observed, which has not been reported before with phenol-formaldehyde resin. A reduction in contact angle values also occurred with both treatments, which is likely due to the hygroscopic nature of the treatment chemicals.

INTRODUCTION

Flammability, which is often considered the biggest disadvantage of wood products in built environments, can effectively be reduced with the utilization of fire retardant chemicals. Most recent studies on the subject have focused on the development of more durable and leach resistant systems, which is the main issue with many of the current chemicals. However, only limited information is available on their effects on adhesion.

The most common fire retardant chemicals already have a long history of use. They include those based on boric compounds, silica, phosphorous, nitrogen and their synergistic combinations. Combinations of phosphorous- and nitrogen-based systems present effective synergism by enhancing fire performance of the two individual components. One common example of phosphorous-nitrogen containing fire retardants is diammonium phosphate (DAP), which under exposure to heat decomposes to ammonia and phosphoric acid. Phosphoric acid releases water and ammonia together with water dilutes the volatile pyrolysis gases (Lowden & Hull 2013; Östman & Tsantaridis 2016). The most explored form of silicon-based flame retardants are probably those based on silicon dioxides, also known as silicates. They are typically introduced to wood in an alkali form, the most common example being sodium silicate (SS; Na_2SiO_3), which is also known as water glass. In fire retardant formulations, SS functions by forming a heat barrier of accumulating inorganic silica residues on the wood surface. This residue functions as an insulating, porous barrier that prevents the release of the volatile pyrolysis products and also reduces the amount of heat that is transferred back to the wood substrate (Mai & Militz 2004; Lowden & Hull 2013). Many fire retardants for lignocellulosic materials work by promoting char formation at lower temperatures, as char has a thermal conductivity several times lower than wood (Kozlowski & Wladyka-Przybylak 2000).

Modification with fire retardant chemicals is known to affect wood material properties in several ways. It may disturb adhesion of wood surfaces by blocking direct contact between the wood substrate and adhesive. Distinguishing the actual chemical effects of fire retardant chemicals on the formaldehyde glue bond formation is challenging because of the complexity of the polymerization reaction. However, at least in the case of inorganic salts such as DAP, it has been suggested that formation of acidic products during thermal degradation of the chemical may prevent curing of phenolic resins, which are generally alkaline substances. Changes in the hygroscopicity of wood material is also a common side effect of many fire retardant chemicals, which may affect the adhesive bond formation. Optimal wettability is crucial for excellent adhesion performance. However, the real bond quality can only partially be predicted from wettability analysis. Contact angle measurement is a useful index in evaluating adhesion, but mechanical testing is the only method for obtaining reliable information about adhesion (Frihart & Hunt 2010)

EXPERIMENTAL

Material information

The wood material used was 0.8 mm thick rotary cut silver birch (*Betula pendula* Roth) veneer, cut to dimensions of 116 x 112.5 mm^2. Two different chemicals were used for the modifications: SS (Merck, 60-w% extra pure aq. solution) and DAP (Merck, ≥99%). From both, 30-w% aq. solutions were prepared and used to impregnate the wood material. Impregnation was carried out in a vacuum-oven by applying 50 mbar absolute pressure for one hour at room temperature. The treated veneers were dried at 103 ^{0}C for 24 hours and conditioned in 25 °C and 30% RH prior to testing.

Thermogravimetric analysis

Thermal degradation of the veneer material was assessed by thermogravimetric analysis (TGA), using a Thermo Gravimetric Analyzer Q500 TGA (TA Instruments) device. The samples were ground in a Wiley mill to pass through a1 mm mesh and 10-15 mg of wood powder was used in the analysis. The measurements were carried out under nitrogen gas at purge rate of 60 ml/min and heating rate of 10 °C per minute until reaching 600 °C. The mass loss was recorded as a function of temperature, and the onset point, temperature at the maximum rate of decomposition and the final amount of residue were determined.

Fire resistance

Fire resistance was studied based on the procedure described by Pries and Mai (2013), where the samples were clamped into a holder and placed on top of a balance. They were positioned so at an angle of 45° to the vertical and ignited from the tip of the sample. The flame height, strength and distance from the sample during ignition were kept constant and mass loss against time was recorded. The duration of both flaming and glowing combustion was also determined visually.

ABES

Bonding of the veneers was evaluated in an automated bonding evaluation system (ABES, Adhesive Evaluation Systems, Incorporated), using a phenol-formaldehyde resin (Prefere 14J025, Dynea Chemicals Oy, Finland). 8.6 µl drop of the resin was dispensed on the sample, and using another sample spread evenly to an area of 20 x 5 mm^2, which corresponds to an adhesive load of 100 g/m^2. As soon as the spreading was finished, the glue line was pressed at a pressure of 2 MPa with the heating plates set to 130 °C. Four different press times were used: 60, 100, 140 and 180 seconds, which enabled observation of the behaviour of the adhesive over longer press times. Shear strength in the grain direction was measured immediately after pressing by the device.

Contact angle analysis

To assess the wettability of the samples by sessile drop method, contact angle measurements were carried out with Cam 200 Optical Contact Angle Meter (serial number 7238, KSV Instruments Ltd) device, using distilled water as probe fluid. The samples were set on an adjustable table and a droplet of water was dispensed to the sample surface. The adsorption of the droplet was recorded with a high-speed camera across the grain line. The droplet volume used was 6.7 µl and each sample was filmed for three minutes or until the droplet was completely adsorbed by the surface. Contact angle values were calculated according to Young’s modulus with CAM2000 software.

RESULTS AND DISCUSSION

Analysis of the thermal properties of modified veneers

Thermal analysis revealed that SS and DAP had an effect on how the veneer pyrolysis proceeded. Results from TGA testing of unmodified reference, DAP and SS impregnated veneers, and pure chemicals themselves and are summarized in Table 1. The effectiveness of fire retardant chemicals can be evaluated from TGA data through a decrease in the value of the onset point, T_{onset}, the temperature of maximum rate of decomposition, T_{max}, and also from an increase in the amount of produced charcoal, which is an indirect indicator of reduction in the amount of combustible gases produced in the process (Rowell 2013).

Table 1: TGA results for unmodified reference DAP and SS impregnated veneers and pure chemical used in the treatments.

Sample	T_{onset} (°C)	T_{max} (°C)	Residue (%)
Reference	257	362	13.1
SS impregnated	257	305	33.5
DAP impregnated	238	278	30.5
Pure DAP (s)	146	600	31.3
Pure SS (aq.)	116	129	36.4

TGA analysis revealed that sodium silicate had no effect on the T_{onset}, which remained on the level of the reference. However, SS effectively lowered T_{max} compared to reference and therefore shifted the pyrolysis pathway at least partly to lower temperatures. An increase in the amount of residual mass (RM), was also observed for SS modified veneers. To evaluate the impact of fire retardant chemicals on the char yield, the residual mass (RM) of the samples was compared with the RM of pure chemicals and reference. For SS modified samples, a notable increase in the RM was observed. The calculated theoretical RM values of SS modified samples did not compare with the actual measured value: RM of SS modified veneers was not equivalent to the sum of the wood char and incorporated chemical. This may indicate that increased char formation took place, which enabled protection of the wood substrate.
Modification with DAP effectively lowered both T_{onset} and T_{max} even more than SS, indicating an improved fire performance by shifting the overall pyrolysis to a lower temperature range. DAP also increased the amount of RM compared to unmodified veneers, but the char yield analysis revealed no signs of increased char formation taking place. The results from TGA were in line with those obtained from the actual fire resistance test, which revealed a reduction in mass loss for the modified samples, as presented in Figure 1.

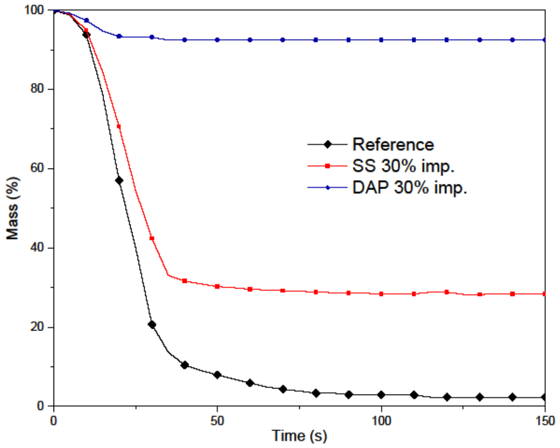

Figure 1: Mass loss of unmodified reference and DAP and SS impregnated veneers in fire resistance test.

Reference samples decomposed completely in the fire resistance test, resulting in nearly 0 % RM. DAP modification inhibited the ignition almost completely, resulting in 93 % RM. Notable charring occurred close to where the source of ignition was placed, but no flaming or glowing combustion took place after the source was removed. SS modified veneers were strongly charred in the test, which supported the char yield results from TGA. The amount of RM (29 %) was notably lower than with DAP, but the samples remained physically almost intact during testing. The observed duration of flaming combustion of the SS modified veneers was nearly the same as that of reference. Interestingly, the glowing combustion time was prolonged by the SS modification, although the variation was notably higher than with other samples.

Wettability and adhesion of the modified veneer material

As can be seen from Figure 2a, DAP and SS modifications lowered the contact angle value compared to the reference, evidencing an increased wettability of wood material. This was most visible with SS impregnated samples, which completely absorbed the water droplet and also presented the highest amount of variance in the results. DAP modification also decreased the contact angle of treated samples. This was to be expected, as most alkaline silicate treatments and inorganic salts are known to increase the hygroscopicity of wood material (Mahltig *et al*. 2008; LeVan & Winandy 2007).

The results from ABES testing are presented in Figure 2b. SS modification decreased the glue bond strength. This was likely due to the formation of a ceramic layer on the veneer surface, which prevents direct contact between the adhesive and the wood substrate. As was noticed in TGA testing, thermal degradation of pure SS took place already at 116 °C, so improvement of the glue bond over the longer press times may be due to gradual SS degradation, which eventually allows a better adhesion to take place. Interestingly, DAP in turn improved the glue bond strength of the veneers. Based on literature, it was assumed to have a very small improvement on the glue bond or even weaken it. DAP releases phosphoric acid during heating, which is believed to prevent the setting of phenolic resins and to weaken the wood material. The slightly alkaline pH-value of DAP solution (8.5) may have promoted the glue bond formation, as the synthesis and curing reactions of phenol formaldehyde take place at basic conditions, and DAP had not yet decomposed into a product of lower pH (Kline *et al*. 1946). However, further work is needed to determine the actual mechanism behind the phenomena and investigate the potential of DAP in improving the adhesion along with fire performance of veneer products.

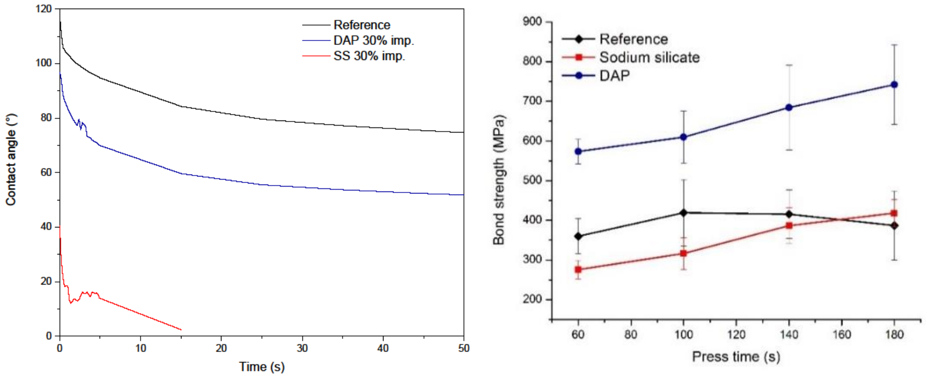

Figure 2: a) Contact angle results of DAP and SS impregnated veneers by the sessile drop method. b) Glue bond strength results of DAP and SS impregnated veneers in ABES testing.

CONCLUSIONS

The results from thermal analysis of DAP and SS modified veneers supported each other. DAP proved to have superior fire resistance and shifted the pyrolysis pathway of wood to lower temperatures in the TGA, which is an indicator of increased fire resistance. In actual fire resistance testing, it also visibly promoted the char formation of the veneers. SS also performed relatively well by increasing the amount of residual mass after combustion.

Both modifications lowered the contact angle values compared to the reference, which was to be expected with SS and DAP modifications, as they were known to increase the moisture content and therefore the hygroscopicity of wood. Glue bond strength of impregnated veneers was determined by ABES, where the glue bond strength of DAP modified samples exceeded that of the reference. Overall, the adhesion and wettability characteristics of fire retardant modified veneer remain poorly understood, which leaves room for further research.

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Natural Weathering and Photostability of Wood Modified by Fatty Acid Esters

Mohamed Jebrane[1] Nasko Terziev[1] and Ivo Heinemaa[2]

[1]Department of Forest Biomaterials and Technology/Wood Science, Swedish University of Agricultural Sciences, Box7008, 750 07 Uppsala, Sweden,[e-mail: mohamed.jebrane@slu.se]

[2]National Institute of Chemical Physics and Biophysics, Akadeemia tee 23, 12618 Tallinn, Estonia [email: ivo.heinemaa@kbfi.ee]

Keywords: α-eleostearic acid, chemical modification, fatty acid, photostability, vinyl ester, weathering, wood

ABSTRACT

Polyunsaturated fatty acid vinyl ester was synthesized *via* a transition-metal catalyzed transvinylation reaction between vinyl acetate and fatty acids from Tung oil. The ensuing fatty acid vinyl ester (vinyl α-eleostearate) was characterized by FTIR and NMR spectral analyses and used as reactive reagent for modification of wood veneers. The covalent grafting of polyunsaturated fatty acid moieties onto the wood was achieved through transesterification reaction between wood hydroxyl groups and fatty acid vinyl ester. The transesterification reaction was confirmed by FTIR, ^{13}C CP MAS NMR spectroscopy and the level of modification was estimated by determining the weight percentage gain (WPG). The photostability of modified wood veneers was evaluated by exposing wood veneers to natural weathering in Uppsala (Sweden) during April-May 2018. Upon 5 weeks of exposure to natural weathering, unmodified wood showed quick color changes and degradation of lignin, while modification of wood vinyl α-eleostearate was very effective in suppressing light-induced color changes at wood surfaces.

INTRODUCTION

Wood is a UV sensitive material. Exposed outdoors, wood undergoes rapid color change and breakdown of wood polymers in the surface (Derbyshire and Miller 1981; Evans *et al.* 1996; Evans *et al.* 2002; Jebrane *et al.* 2009). Because of its aromatic nature, lignin strongly absorbs UV light (Kalnins 1966), which leads to radical-induced depolymerisation of lignin and cellulose. Depolymerization of lignin generates unsaturated aromatic compounds, which are yellow in color. Hence, wood exposed outdoors yellows initially and becomes grey when blue-black staining fungi (Salla *et al.* 2012) colonize the white, cellulose-rich surface. To protect wood from photodegradation, a variety of different approaches has been investigated (Evans 2008) including using additives (UV absorbers) (Rabek 1990), chemical treatments (Evans *et al.* 2002, Jebrane *et al.* 2009). However, most of these approaches present many drawbacks, such as involving toxic chemicals, energy inefficiency, and expensive. In recent years, public concern about the environment has led to the creation of regulatory programs to reduce air pollution, increasing the pressure on wood manufacturers to reduce harmful emissions derived from chemical treatments. In this context, huge scientific research on the biobased products in the world has focused on the environmental impacts of continuing using fossil-based materials in diverse industries. Indeed, public concerns related to fossil-based resources have led politicians and administrators at EU and national level to set targets for shifting to low carbon societies by 2050. For achieving this target, the use of materials originating from renewable resources in diverse industries has been pointed out as important strategies to decrease the dependency on fossil-based products. Several attempts have been made for the use of bio-based chemicals to protect wood (Jebrane *et al.* 2014; Kose Demirel *et al.* 2018), but the approaches tested are either expensive or involving multiple steps. In this context, a new method using a bio-based precursor for chemical functionalization of wood has been developed.

In this study, thin Scots pine (*Pinus sylvestris* L.) veneers were chemically modified (esterified) with polyunsaturated fatty acid vinyl ester and the photostability of the modified wood was assessed. Tung oil was hydrolyzed and the obtained fatty acids were chemically functionalized with vinyl acetate and used to react with hydroxyl groups in wood. Preliminary experimentation had shown that the vinyl ester form of triply conjugated fatty acid (vinyl α-eleostearate) reacted with wood veneers producing esterified wood. Furthermore, it was assumed that the introduction of naturally triply conjugated fatty acid moieties into the wood cell wall might act as a UV screen protecting lignin and cellulose from photodegradation.

EXPERIMENTAL

Wood treatment

Scots pine sapwood veneers of 1 mm × 10 mm × 100 mm (along the grain) were cut from the radial face of defect free wood blocks. Prior to modification, all veneers including unmodified controls were extracted in a Soxhlet apparatus with a mixture of toluene: ethanol (2:1/v:v) for 8 h, and then with water for an additional 6 h, to remove all extractives. Wood veneers were then oven-dried at 103°C for 16 h and cooled to ambient temperature in a desiccator. Dried veneers were treated with vinyl α-eleostearate in a reaction tube using catalyst K_2CO_3 and solvent N-methyl-pyrrolidone (NMP) at 100°C for different reaction durations. Vinyl α-eleostearate was synthesized from Tung oil following alkaline hydrolysis and according to the procedure described by Jebrane *et al.* (2016, 2017). For each reaction, 10 replicates of veneers were reacted together for 3, 6 and 9 h in a solution containing the vinyl ester, K_2CO_3 (catalyst) and NMP. After reaction, the esterified veneers were Soxhlet extracted with water for 2 h and then with acetone for an additional 8 h to remove non-bonded chemicals. The weight percentage gains (WPGs) of modified and extracted veneers were then calculated.

Evaluation of photostability of esterified veneers

The photostability of modified and unmodified veneers was assessed using natural weathering. Five veneers from each 10 modified veneers for the three different WPGs (3, 6 and 9 h) were selected at random, placed against glass backing plate and clamped lightly at their ends. The glass plate containing 15 esterified veneers (three different WPGs) and 5 unmodified samples were exposed outdoors for 5 weeks in Uppsala during the April-May of 2018. The glass plate was oriented horizontally and facing south to maximize the total UV radiation received by veneers. The veneers were removed from the weathering at regular interval (one week), the color was measured at four different locations for each sample, and average values were calculated. After weathering, veneers were oven-dried as above and the chemical changes were measured.

Analytical techniques

ATR–FTIR spectra of oil, fatty acid, fatty acid vinyl ester (vinyl α-eleostearate) and wood samples were acquired in the range of 4000–450 cm^{-1} (spectral resolution 4 cm^{-1}, 16 scans) on a Perkin Elmer Spectrum One FT–IR Spectrometer equipped with a Universal Attenuated Total Reflectance Accessory (UATR).

Solid state ^{13}C CP MAS NMR spectra of modified and unmodified wood samples were obtained at room temperature on a Bruker Avance–II spectrometer operating at 150.9 MHz using a custom built MAS NMR probe. The samples were packed into 4 mm Zirconia rotors. Chemical shifts were relative to TMS used as an external standard. For each sample, a total of 20000 scans were accumulated.

Colour measurements: the colour change of modified and unmodified veneers exposed to natural weathering was monitored using Konica Minolta CM-2500d surface reflectance spectrophotometer. Co-ordinates CIELab color i.e. lightness (L), redness (a) and yellowness (b) were measured on each sample before and after irradiation and change in these parameters due to weathering ΔL^*, Δa^*, and Δb^* were calculated. The variables above were measured periodically and shown after 1, 2, 3, 4 and 5 weeks of exposure while spectral analyses of wood were carried out once after 5 weeks of exposure and compared to the control samples.

RESULTS AND DISCUSSION

Chemical synthesis and spectroscopic characterization of wood reagent.

For comparison with the classical acylation of wood with fatty acids by means of acyl chloride, the corresponding long chain vinyl ester was synthesized. Tung oil was hydrolyzed and the ensuing fatty acids were functionalized by transesterification with vinyl acetate in order to obtain vinyl *α*-eleostearate according to the procedure described previously (Jebrane *et al.* 2018). The structure of the new bio–based long chain vinyl ester was confirmed by the combined spectroscopic analyses reported above.

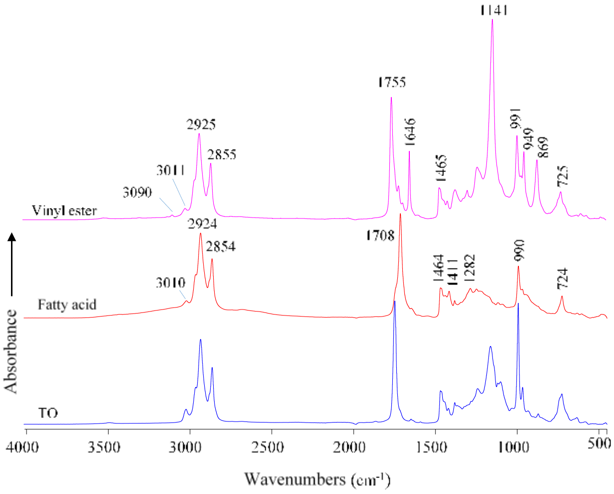

Figure 1: FTIR absorbance spectra of Tung oil (TO), α-eleostearic acid (fatty acid), and vinyl eleostearate (Vinyl ester)

Compared with the FTIR spectra of the starting Tung oil (TO) and Tung oil's fatty acids (FA), the spectra of the synthesized fatty acid vinyl ester showed the emergence of new characteristic absorption bands (Fig. 1). These new absorption bands were observed around 3090 cm^{-1} (vinyl C–H stretching), 3011 cm^{-1} (chain unsaturation C–H stretching), 1755 cm^{-1} (C=O stretching of vinyl ester), 1141 cm^{-1} (ester C–O stretching), 949 cm^{-1} (CH out of plane deformation of $CH{=}CH_2$), 869 cm^{-1} (CH_2 out of plane deformation of $–CH{=}CH_2$). In addition to the appearance of new characteristic bands, a disappearance of carboxyl groups at around 2672 cm^{-1} (OH stretching) and at 1708 cm^{-1} (C=O stretching) was observed, confirming the complete transformation of fatty acid into vinyl ester.

Esterification of wood by fatty acid vinyl ester and spectroscopic characterization.

A polyunsaturated fatty acid was investigated to verify whether this biobased precursor is effective for the photo-stabilization of wood polymers and offer improved mechanical properties and weathering performances owning to provide new biobased alternatives for wood protection. Polyunsaturated fatty acid vinyl ester was chosen as long acyl chain with a naturally triply conjugated fatty acid to increase the hydrophobicity and improve photostability of wood. Wood veneers were modified with the synthesized vinyl ester using a transesterification process. After 3, 6, and 9 h of reaction, WPG's of 6.7, 12.2 and 20.2% were obtained and the grafting of fatty acid moieties into wood was confirmed by FTIR and ^{13}C CP–MAS NMR spectroscopy. Figure 2 depicts the FTIR spectra of unmodified and wood modified with fatty acid vinyl ester. In addition to the prominent carbonyl stretching vibration at 1735–1743 cm^{-1} ($\nu_{C=O}$) and the C–O stretching vibrations at 1157–1230 cm^{-1} ($\nu_{C–O}$), some new characteristic vibrations of the grafted acyl chain moieties were identified namely, the strong skeletal bands of long chain moieties at 2922 and 2853 cm^{-1} ($\nu_{C–H}$), 1370 cm^{-1} ($\gamma_{C–H}$), and 720 cm^{-1} (CH_2 rocking). α-eleostearate–modified wood samples were further characterized by ^{13}C CP MAS NMR spectroscopy (Figure 3). In addition to the dominant pattern corresponding to the carbons of wood (cellulose, lignin), signals for carbons of the newly introduced long chain eleostearate moieties appeared clearly in the α-eleostearate–modified wood spectra. These signals were assigned directly on the spectra of α-eleostearate–modified wood according to the nomenclature given on the associated structure.

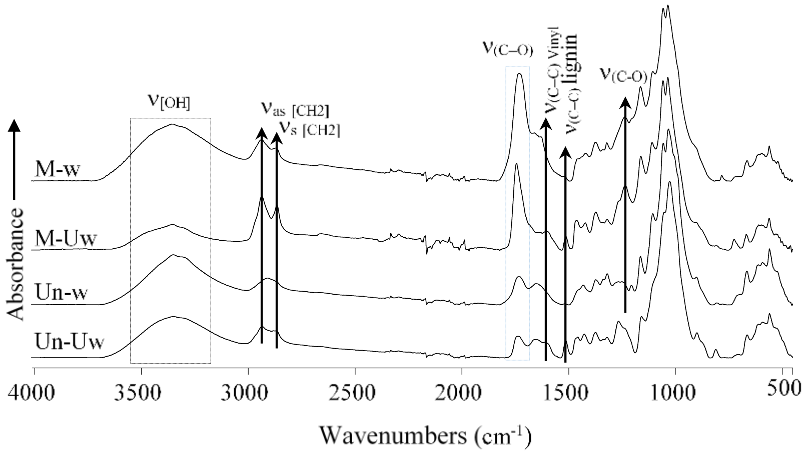

Figure 2: FTIR–ATR spectra of unmodified controls (Un-Uw) and veneers esterified (M) with vinyl eleostearate, before (Uw) and after (w) natural weathering.

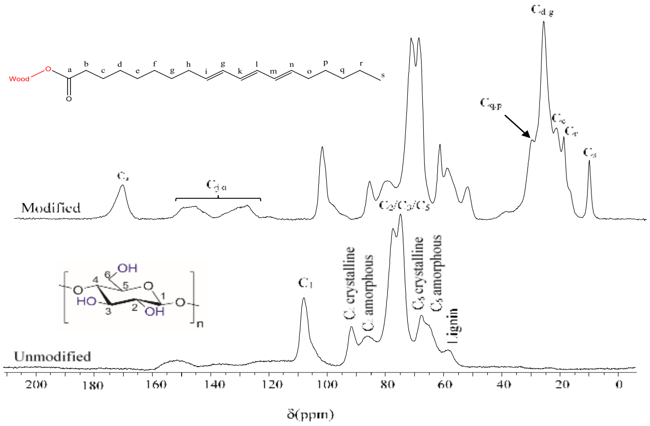

Figure 3: ^{13}C CP-MAS NMR spectra of unmodified controls and veneers esterified with vinyl eleostearate (Modified, WPG 20.3%)

Photostability of modified veneers

Fig. 4 shows the effect of grafting triply conjugated fatty acid moieties onto the wood on colour changes of surfaces of scots pine veneers after five weeks of exposure to natural weathering. The colour of unmodified wood changed rapidly and darkened upon UV light irradiation. After modification, wood veneers become slightly yellower due to incorporation of additional chromophores (triply conjugated fatty acid). Contrary to unmodified wood, modified samples did not darken upon UV irradiation.

The observed colour changes were quantified by measuring CIELab parameters. The colour change observed in unmodified wood after exposure is demonstrated by the decreased value of lightness (ΔL*) and the increased in the yellowness (Δb*) and redness (Δa*) (graph not shown). As expected, the yellowness of unmodified veneers increased progressively after weathering. In contrast, modified veneers became less yellow during weathering irrespective of weight gain due to the grafted fatty acid moieties. Similar results were reported in the literature (Evans *et al.* 2002; Jebrane *et al.* 2009; Sèbe *et al.* 2009; Nagarajappa and Pandey 2016). The increase in yellowness of veneers upon irradiation indicates photo yellowing of wood surfaces due to photodegradation of lignin (Δb* values increased from 22.7±0.5 to 37.2±0.8 for unmodified wood, but decreased from 38.3±0.3 to 26.5±0.7 for modified wood). The high Δb* value measured for modified wood before weathering is due to the incorporation of additional chromophores into the wood.

Figure 4: Photographs showing changes in colour of (A) unmodified and (B) α-eleostearate–modified wood (different WPGs) after 5 weeks of exposure.

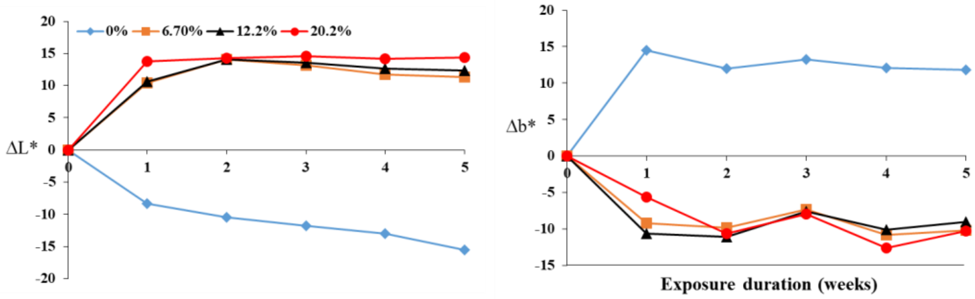

Figure 5: Changes in lightness (ΔL*) and yellowness (Δb*) of unmodified (0%) and α-eleostearate–modified wood (different WPGs) after 5 weeks of exposure.

The chemical changes occurring in unmodified and esterified wood veneers were examined by FTIR–ATR spectroscopy. Infrared spectra of unmodified wood before and after weathering are shown at the bottom of Fig. 2. The most obvious difference between the two spectra is the disappearance of the absorption band at 1509 cm^{-1} (benzene ring stretching in lignin), indicating delignification of weathered samples (Evans *et al.* 2002;

Jebrane *et al.* 2009; Nagarajappa and Pandey 2016) as expected. The IR spectra of modified veneers before and after weathering are shown at the top of Fig. 2. The characteristic vibrations of the grafted fatty acid moieties were easily identified in the FTIR spectra (Fig. 2) (Jebrane *et al.* 2017). After weathering, a decrease in the peak at 1509 cm^{-1} was observed, indicating a delignification of modified veneers during weathering. An increase in the intensity and broadening as well as shifting of the peak at 1735 cm^{-1} was observed after weathering and particularly in modified veneers, indicating a generation of moities containing carbonyl groups. No significant changes were observed in other peaks, indicating less degradation of other wood polymers.

CONCLUSIONS

A process of chemical modification of wood with polyunsaturated fatty acid vinyl ester (vinyl α-eleostreate) has been developed. The process comprises a synthesis of vinyl ester of polyunsaturated fatty acid by the transvinylation of α-eleostearic acid with vinyl acetate, followed by a covalent grafting of fatty acid moieties onto the wood via transesterification reaction between wood hydroxyl groups and the synthesized vinyl α-eleostreate. Under studied conditions, WPGs ranging from 7 to 20 % was achieved, indicating that a significant amount of chemicals remained bonded in the wood. Weathering test indicates that the modification is very effective at protecting wood against photo yellowing and UV degradation of wood polymers.

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Effects of thermal modification on bending properties and chemical structure of Iroko and Padauk

Michal Kroupa[1], Milan Gaff[2], Olov Karlsson[3], Olena Myronycheva[4], Dick Sandberg[5]

[1]Department of Wood Processing, Czech University of Life Science in Prague, Kamycka 1176, Praha 6-Suchdol, 16521 Czech Republic [email: majkykroupa@gmail.com]
[2]Department of Wood Processing, Czech University of Life Science in Prague, Kamycka 1176, Praha 6-Suchdol, 16521 Czech Republic [email: gaff@fld.czu.cz]
[3]Division of Wood Science and Engineering, Luleå University of Technology, SE-93187 Skellefteå [email: olov.karlsson@ltu.se]
[4]Division of Wood Science and Engineering, Luleå University of Technology, SE-93187 Skellefteå [email: olena.myronycheva@ltu.se]
[5]Division of Wood Science and Engineering, Luleå University of Technology, SE-93187 Skellefteå [email: dick.sandberg@ltu.se]

Keywords: bending properties, *Milicia excelsa*, *Pterocarpus soyauxii*, thermal modification, bendability, modulus of rupture, extractives, phenols, pH, Ec, ash

ABSTRACT

The thermal modification process essentially involves a controlled degradation of the wood, primarily resulting in the degradation of hemicelluloses. In this study, thermal modification at temperatures of 160, 180 and 210 °C was used in superheated steam. Examined wood samples were iroko (*Milicia excelsa* (Welw.) C.C. Berg) and padauk (*Pterocarpus soyauxii* Taub.). Testing of bending properties was done according to the Standard ČSN 49 0116 (ASTM 04.10 WoodD143-09). The samples were loaded by three-point bending. Chemical analysis of total extractives and phenols content, pH and Ec changes and ash content.

The results show that with the increasing temperature of the thermal modification process, the modulus of rupture and density decreases. The force and deflection at the limit of proportionality increased. The thermal modification process affected the chemical characteristics of both species. The distribution of total extractives and phenols varied strongly for iroko, but for padauk decrease with increased treatment temperature and time was observed. Having a more detailed assessment of wood chemical changes and degradation products from structural and non-structural wood components and their resistance to biological attack is necessary for the future development of sustainable technologies for the thermal treatment of iroko and padouk.

INTRODUCTION

Commercial tropical timber species such as iroko (Milicia excelsa (Welw.) C.C. Berg) and padauk (Pterocarpus soyauxii Taub.) possess increasing demand in various wood products applications (International Tropical Timber Organization (ITTO) 2018a, b) that requires to develop modern timber processing technologies. Iroko is widespread in tropical and subtropical Africa. The colour of Iroko is usually yellow to golden or medium brown. It is very durable and resistant to rot and insect attack. Padauk can be found in central and tropical west Africa. Its colour can vary, ranging from pale pinkish-orange to deep brownish red. Padauk has excellent decay resistance and is rated as a durable to very durable species. It is also resistant to termite attacks and of another type of insect attack.

The colour and texture are favoured to use these two wood species in musical instruments, luxury furniture and other high-value products. However, new information came that extractive rich padauk wood species can have a negative impact on human health and cause dermatitis and allergic reactions via dust dispose of (Kiec-Swierczynska *et al.* 2004). For softwood species, it has been shown that thermal modification can reduce the number of extractives and lead to the formation of less toxic substances (Poncsak *et al.* 2009; Esteves *et al.* 2011).

Thermally modified timber (TMT) is, according to CEN (2007), wood at which the composition of the cell wall material and its physical properties are modified by exposure to a temperature higher than 160ºC and conditions of decreased oxygen availability. The wood is altered in such a way that at least some of the wood properties are permanently affected through the cross-section of the timber. This product is related to heat-treated wood, but to distinguish it from heat sterilisation at a lower temperature (≈55°C) with the purpose of killing pests in solid wood materials and preventing their transfer between continents and regions. Main disadvantage of thermal modification is loss of strength due to the degradation of wood constituents such as extractives, however, as advantages the biological resistance against some micro-organisms and insects could be improved, swelling and shrinking reduced up to 50-90 % and equilibrium moisture content could be reduced too (Karlsson *et al.* 2012, 2014; Navi and Sandberg 2012).

For many tropical species, there is a lack of information about changes in properties during thermal modification. Therefore, the purpose of this study was to understand the influence of thermal modification on bending properties and changes of chemical structure of iroko and padauk.

EXPERIMENTAL

Iroko (*Milicia excelsa* (Welw.) C.C. Berg) and padauk (*Pterocarpus soyauxii* Taub.) was harvested in Gabon (Sablík *et al.* 2016). The dimension of specimens was 20 x 20 x 300 mm. Moisture content before thermal treatment was 3±1%. Thermal modification achieved according to ThermoD® (International Thermowood Association 2003) process in the thermal chamber with filled kiln capacity 0.8 m^3.

The scheme of technological parameters of thermal modification process provided in Table 1.

Table 1: Scheme for thermal modification

Test group No.	**Heating**		**Thermal modification**		**Cooling**		**Total time [h]**	**No. of specimens**
	Time [h]	**Temp[°C]**	**Time [h]**	**Temp[°C]**	**Time [h]**	**Temp[°C]**		
				Iroko				
1	0	20	0	20	0	20	**0**	30
2	11.6	160	3.0	160	3.9	50	**18.5**	30
3	14.8	180	3.0	180	5.8	50	**23.6**	30
4	18.6	210	3.0	210	7.2	50	**28.8**	30
				Padauk				
5	0	20	0	20	0	20	**0**	30
6	10.0	160	3.0	160	2.3	50	**15.3**	30
7	11.7	180	3.0	180	4.1	50	**18.8**	30
8	15.1	210	3.0	210	4.5	50	**22.6**	30

Testing of bending properties has been done according to the standard ČSN 49 0116 (ASTM 04.10 WoodD143-09). The samples were loaded by three-point bending in a universal testing machine UTS 50 (TIRA, Germany) according to EN 310. The loading speed was 3 mm/min. Loading forces were measured using data logger ALMEMO 2690-8 (Ahlborn GmbH, Germany).

The data used to create a force-deformation diagram, in which we applied the method of accurate identification of boundary points developed by authors (Gaff *et al.* 2016, 2017). The parameters used for analysis: force at the limit of proportionality $\mathbf{F_E}$, deflection at the limit of proportionality $\mathbf{Y_E}$, force at the modulus of rupture $\mathbf{F_P}$, deflection at the modulus of rupture $\mathbf{Y_P}$. The evaluating bendability did by using the minimum bend radius and coefficient of bendability. The minimum bend radius $\mathbf{R_{minB}}$ and the coefficient of bendability $\mathbf{K_{bendB}}$ are based on the bending geometry. The minimum bend radius $\mathbf{R_{minC}}$ and the coefficient of bendability $\mathbf{K_{bendC}}$ are based on the basic bending equation (Gaff *et al.* 2016).

For the assessment of the chemical changes during thermal modification process the extraction of extractives for the total amount was done in mini-Soxhlet extractor by acetone/water 95:5v/v and evaluated gravimetrically by percentage of the dry mass of wood (Willför *et al.* 2006). The total phenolics content was determined by Folin-Chiocalteu assay (Julkunen-Tiitto 1985). The absorption was measured after 20 minutes at 735 nm against zero absorbance. Tannic acid (VWR Chemicals; 83510.260) was used for the standard curve, and the results are expressed in mg of tannic acid per gram of dry mass of wood (mgTA/g dry w.). The measurement of pH and Ec was done by pH meter Metrohm 744 after treatment of the sample with a sodium chloride solution to exchange protons in less accessible carboxylic groups in the wood by sodium ions (Sithole 2005). The ash content of the wood was determined gravimetrically after heating at 560°C in a muffle furnace and expressed in percentage of the dry mass of wood. The effect of individual factors evaluated using ANOVA, specifically utilizing Fisher’s F-test in STATISTICA 12 (Statsoft Inc., USA) and IBM SPSS 20 software (IBM 2014).

RESULTS AND DISCUSSION

The thermal modification of iroko and padauk affect the mechanical properties and chemistry of the wood significantly. The increasing processing time reduces the modulus of rupture and density but increases the values of force and deflection at the limit of proportionality. However, some increasing trend of the $\mathbf{F_P}$ is evident for the temperature of 160°C.

The average values of the monitored mechanical characteristics listed in Table 2.

***Table 2: Mean values** of the Y_E, Y_P, F_P, F_E, RminB, RminC, KohB, Kohn*

Thermal Modification	Y_E [mm]	Y_P [mm]	F_P [N]	F_E [N]	Density [kg/m^3]
			Iroko		
20	2.0	5.0	2079	996	615
160	3.1	4.7	2180	1542	593
180	3.0	4.5	2015	1518	591
210	2.7	3.3	1397	1181	594
			Padauk		
20	2.6	6.0	3262	1749	676
160	3.7	5.4	3314	2346	691
180	3.4	4.5	2805	2174	797
210	1.7	3.7	1875	1245	657

Thermal Modification	RminB	RminC	KohB	KohC
		Iroko		
20	1400	1007	0.01	0.02
160	1555	1042	0.01	0.02
180	1610	1079	0.01	0.02
210	2210	1379	0.01	0.02
		Padauk		
20	1346	789	0.02	0.03
160	1373	920	0.01	0.02
180	1647	1103	0.01	0.02
210	1996	1336	0.01	0.02

The data about changes of some chemical properties for thermally treated timber presented in Table 3. The total extractives and phenols in untreated wood in our samples corresponds to previously studied data (Saha *et al.* 2013; Nagawa *et al.* 2015). It is well known that increasing temperature in thermal modification process affects the significantly chemical composition of the wood. The distribution of total extractives and phenols varied strongly for iroko but was relatively low at the most extensive treatment (Table 3). For padauk, the decrease in the amount of extracted phenols with treatment temperature and time was strongly evident. The unexpected phenomenon of similar pH was observed for padauk wood with an elevation of the thermal treatment time and temperature (Table 3). A significantly lower pH has been found in thermally modified than in untreated birch (O. Dagbro *et al.* 2011). In case of iroko, pH was in similar range as for birch, but the thermal treatment of iroko did not reduce the pH. A fairly high content of ash was found in the iroko samples (Table 3). Higher pH and ash content for iroko could be explained by biomineralization properties of that tree that leads to accumulation of mineral carbon. Calcium carbonate has been found in Iroko (ref) and such compound could work as a buffer agent for the formed acids during the thermal modification process (Cailleau *et al.* 2004).

Table 3: Results of chemical tests

Thermal modification	Total extractives [%]	Total phenols [mgTA/g dry w.]	pH	Ec	Ash content [%]
Iroko					
20	7.8	27.5	5.5	108.0	2.0
160	10.4	30.4	5.3	118.7	2.3
180	8.1	24.6	5.2	127.7	1.9
210	4.8	11.8	5.2	126.0	1.9
Padauk					
20	11.1	27.4	3.7	213.7	0.2
160	9.9	27.1	3.7	213.3	0.2
180	9.5	22.5	3.8	208.3	0.3
210	7.5	22.0	3.8	205.0	0.4

CONCLUSIONS

In our study, we found that thermal modification process significantly affects bending properties and acetone soluble extractives, phenols and ash content of iroko and padauk wood as well as pH. The more detailed assessment of wood chemical changes and degradation products from structural and non-structural wood components and resistance to biological attack seems to be a reasonable step for future development of the sustainable technology of iroko and padauk thermal treatment.

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Modified wood in actual use and its weathering performance after outdoor exposure

Ville Lahtela[1,2] and Timo Kärki[2]

[1]Lappeenranta University of Technology, RE-SOURCE – Research Platform, P.O. Box 20, Lappeenranta, FINLAND [email: ville.lahtela@lut.fi]
[2]Lappeenranta University of Technology, Fiber Composite Laboratory, P.O. Box 20, Lappeenranta, FINLAND [email: timo.karki@lut.fi]

Keywords: Modification, impregnation, heat treatment, melamine, sodium silicate

ABSTRACT

Modification of wood has become increasingly significant in recent years, and a number of modified wood products are available. Some inherent qualities of wood, such as greying, may raise concerns about the durability of modified wood. This study investigates the weathering properties of modified wood products in actual use. Two commercial modified wood materials and two possible contenders of our own production were selected for the study. In accordance with the instructions of the architect, “stadium stairs” were built in 2014 by using various modified wood products. The stairs have been in actual use in a new residential area for nearly three years, and their resistance to weathering were analysed through measurement of the surface colour with a spectrophotometer. The result showed that weathering had caused notable and interesting differences among the modified wood materials. It is concluded that each of the modified wood products showed individual resistance against to greying.

INTRODUCTION

Natural resources, such as forests and wood, have a remarkable influence and contribution to humankind and the economy. For example, forest areas cover a large share of the total land area, and millions of people across the world are employed by the forest sector. The importance of wood material will be emphasized in the future with the increasing population and growing economies. Therefore, it is important to use and utilize wood material in accordance with sustainable development. One popular application for wood material is use in outdoor conditions. Wood has a number of favourable properties, but also some inherent properties which have created a demand for developing wood properties by modification technology. The modification of wood material is an excellent way to meet the idea of sustainable development. Various methods of wood modification are known and several studies have been performed on the topic. We have combined two general wood modification methods, impregnation and heat treatment, and studied various properties of wood. The results of these properties after laboratory tests have been published in scientific articles, and collectively in the doctoral dissertation of Lahtela (2016). However, studies on the properties of the material in actual use have not been published previously. Therefore, the aim of this paper is to introduce the weathering performance of modified wood material in outdoor exposure.

EXPERIMENTAL

In this study, a set of stadium stairs (Fig. 1) was built from various modified wood materials, including two commercial modified products and two possible contenders of our own production. The commercial modified wood products were Q-Treat (treated with sodium silicate and thermal modification) and ThermoWood (treated with thermal modification), and they were purchased from a retailer. In addition, Scots pine (*Pinus sylvestris* L.) and Larch (*Larix sibirica* L.) wood material were impregnated with a melamine solution, at a pressure of 10 bars for 120 min. The result of the impregnations was measured by weight percent gain (WPG).

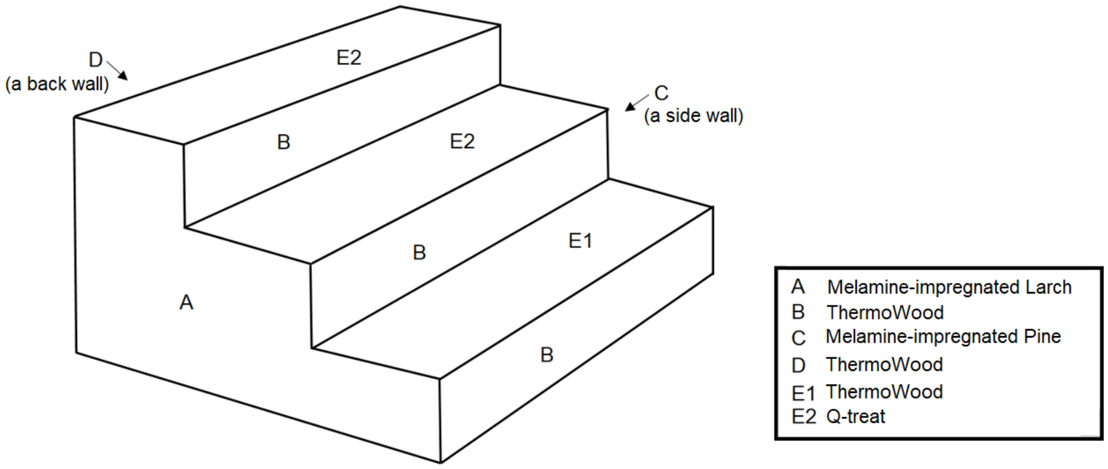

Figure 1: Instruction for stadium stairs and location of modified wood material

The stadium stairs were utilized at various events in a new residential area in Suurpelto, Espoo, Finland. Suurpelto Garden City is a new residential area of 325 hectares in the middle of Espoo, where housing and construction follow the principle of sustainable development and nature is valued. The construction started in 2007 and the area will continue to be built until 2025. The set of stairs was placed in an open space near the Info Pavilion Building of Suurpelto (60.18709N, 24.74209E). The stairs were weathered from June 2014 to the end of April 2017 for a total of 35 months. The typical weather conditions in Espoo for the duration of the exposure are presented in Table 1. The colour measurements were performed at the beginning and the end of the test.

Table 1: Average weather conditions in Espoo for the duration of exposure (FMI 2018)

Month	**2014** **rain^1 / T^2**	**2015** **rain^1 / T^2**	**2016** **rain^1 / T^2**	**2017** **rain^1 / T^2**
January		68.9 / -1.1	52.6 / -9.2	30.5 / -2.2
February		41.4 / 0.7	79.4 / 0.1	28.6 / -2.3
March		57.6 / 1.8	11.6 / 0.5	39.3 / 0.9
April		57.3 / 5.3	73.5 / 4.5	33.2 / 2.5
May		43.9 / 9.2	11.7 / 13.4	
June	91.8 / 13.2	81.9 / 13.3	119.5 / 15.0	
July	13.6 / 19.2	81.8 / 16.0	67.6 / 17.4	
August	143.5 / 17.1	53.4 / 16.5	96.2 / 15.8	
September	59.9 / 11.9	68.8 / 12.7	72.1 / 12.5	
October	44.5 / 6.3	20.7 / 5.3	23.3 / 5.1	
November	50.2 / 2.9	70.2 / 5.1	80.0 / -0.4	
December	83.0 / -0.4	66.8 / 2.8	18.8 / -0.1	

^{1}*Monthly total amount of rainfall (mm)* ^{2}*Monthly average temperature (°C)*

Colour measurements

The surface colour of the studied materials was measured with a Minolta CM-2500d spectrophotometer (Konika Minolta Sensing Inc., Japan) with the following settings: illumination D65, observer 10°, and illumination area 8 mm. The colour change was measured according to the CIELAB system, measuring simultaneously including (SCI) and excluding (SCE) the influence of gloss in one measurement. The CIELAB system is based on a three-dimensional colour space with L*, a*, and b* coordinates, representing coordinates from white to black, red to green, and yellow to blue, respectively. The colour difference is calculated by the following equation (Eqn. 1):

$$\Delta E^* = \sqrt{(\Delta L^*)^2 + (\Delta a^*)^2 + (\Delta b^*)^2} \qquad (1)$$

Where $\Delta L*$, $\Delta a*$, $\Delta b*$ represent the differences between the initial and final values of L*, a*, and b*, respectively. The colour measurement of melamine-impregnated samples consisted of 18 measurement points per quality, locating in the vertical direction. The colour measurements of Q-Treat wood included 16 measurements in the horizontal direction. The colour measurements of ThermoWood included in total 26 measurements in vertical and horizontal directions.

RESULTS AND DISCUSSION

The WPG values of melamine-impregnated Scots pine and Larch were 24.93 and 5.57, respectively, with remarkable high standard deviations, 14.13 and 5.18, indicating heterogeneous nature of the wood material. The different impregnation results between wood species showed that wood material had a significant effect on the penetration.

The colour differences ($\Delta E*$) after weathering outdoor exposure are presented in Figure 2 as a bar chart with standard deviations as error bars. The melamine-impregnated Pine and Larch had a slightly lower colour change compared to the commercial examples of modified wood (Q-Treat and ThermoWood). However, the commercial modified wood had a smaller deviation in the average results. Comparison between SCI and SCE showed that gloss of did not have a significant role in the results of weathering performance of the modified wood material.

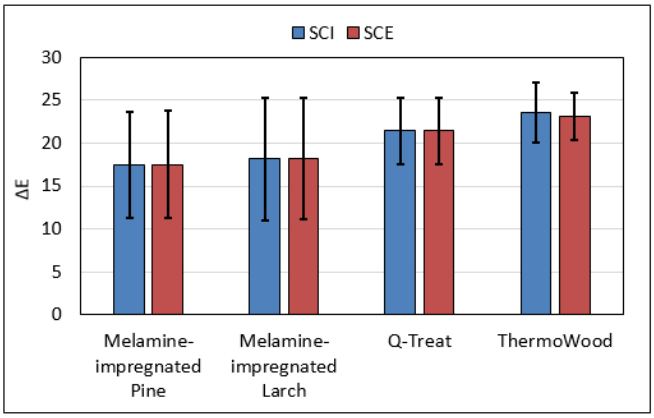

Figure 2: Total colour alteration (ΔE) of modified wood products during the test periods.

Wood components are sensitive to weathering in different ways. For example, lignin is sensitive to ultraviolet radiation and it begins to degrade within a short time (Williams 2010). It has been found that melamine resin can depose in the cell wall structure surrounding the area of lignin, and it acts possibly as a diffusion-hindering matrix and delays lignin decay (Müller and Steiner 2010).

Figure 3: Just-built stairs ready for transport (top) and the stairs after 35 months actual weathering exposure in Suurpelto (below).

The stadium stair were in actual use of the inhabitants and were moved as needed. Therefore, a certain compass point for the wood material cannot been determined. However, the ThermoWood samples were located on the horizontal and vertical directions on both front and back walls, but the colour change measurements were quite similar in spite of the point or location direction.

CONCLUSIONS

The weathering performance of the modified wood materials in actual use were investigated in this work. A lot of work with wood modification has been done in laboratory conditions, but results from the field are few, which could also contribute to the agenda of wood modification. Some preliminary conclusions can be drawn from the results. The gloss did not seem to have significant role, but the melamine-impregnated wood material showed slightly improved weathering performance compared to the commercial examples. The relatively high deviations meant that heterogeneous nature has to be tolerated in wood material. The study demonstrated that melamine impregnation is able to challenge the current modified wood products available in the market as regards weathering performance.

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Performance of thermal modified radiata pine in real cases of facades and deckings in North Spain

David Lorenzo[1] , Alfonso Lozano[2], Juan Fernández-Golfín[3], Manuel Touza[4] and René Herrera[5]

[1]Engineering for Rural and Civil Development, University of Santiago de Compostela, Campus de Lugo 27002, Spain [email: davidlorenzofouz@gmail.com]

[2]Construction Engineering Area, EPI, Edificio Oeste nº 7, Campus de Gijón E-33203 Gijón, Spain [email: alozano@uniovi.es]

[3]Forest Research Centre (CIFOR) National Institute for agricultural and Food Research and Technology (INIA), 28080 Madrid, Spain [email: golfin@inia.es]

[4]GAIN CIS-Madeira, Galicia Technological Park, 32901 San Cibrao das Viñas, Ourense, Spain [email: manuel.cesareo.touza.vazquez@xunta.gal]

[5] Chemical and Enviromental Engineering Department, University of the Basque Country, Plaza Europa 1 20018, San Sebastian Spain [email: reneherdiaz@gmail.com]

Keywords: Decking, facade, modified, performance, radiata, Spain, thermal

ABSTRACT

This paper describes Spanish projects with thermal modified radiata pine (*Pinus radiata*) in facades and deckings as friendly building material. In exterior wooden uses, there is a risk of degradation, implicit to each geographical location, local climate and inherent wood material variables as well as design details (sheltering, distance from ground, moisture traps, exposure to wind-driven rain, physical protection, etc.), coatings and maintenance. In short, all these factors could generate changes to the wood material due both to biological and abiotic agents. The most important problems in exterior wooden uses are the risk of decay by wood destroying fungi as well as aesthetics concerns (discolorations, moulds, wood disfiguring fungi, etc.), cracks and deformations of wood elements. This paper shows the performance of thermal modified radiata pine in different real cases in North Spain, considering the main factors to assess the wood performance status, focusing in each case on thermal modified processes selected and considering geographical location, local climatic conditions and the influence of design details. It is important to identify the parameters influencing in the performance, from simple aesthetic defects to decay problems affecting the thermal wood elements. The examples include some cases of severe exposure under a wet and warm climate as North Spain. These examples also show the important cooperation between the different key actors involved in the projects, including the decision-making process among between the suppliers, architects and the technical assistance. The performance of an exterior wooden project with thermal modified radiata pine strongly depends on the selected material and modification process as well as exposure conditions and construction design. The decision

considering to apply or not a coating and, if is the case, the needed posterior maintenance program is also a key factor in the aesthetic performance.

INTRODUCTION

Across Europe is very common to find thermal modified wood in facades and deckings, most of them used softwood species such as: fir, spruce, larch and pine (Taylor, Kaczmar and Hislop 2013).

In Spain the use of thermal modified wood in facades and deckings, became more and more popular since approximately 2000. This material, in most of cases, is imported from central and northern European origin and production, mainly of softwood species.

In 2011 a Spanish company starts the production of thermal modified wood, using mainly as raw material a local softwood species (*Pinus radiata*), very common in plantations in the North of Spain.

This paper shows some examples of facades and deckings built in the last decade in the North of Spain, using thermal modified *Pinus radiata*.

EXPERIMENTAL

The performance of thermal modified wood in facades and deckings depends on different key aspects Use class, wood species and thermal process selected, detail designs, coating, maintenance and climatic zone and local climate.

Use class

The concept of use class defined in EN 335 (European Committee Standardization 2013) is related to the probability that a wooden element is attack by biological agents and basically depends on difference in environment exposures. Use class indicates a position of the wood element, then a chance of passing sometimes over 20 % moisture content. It is emphasized that the approach really should be considered the period that a wood element remains above 20 % moisture content following CTE (Spanish Ministry of Development 2009).

Regarding facades and deckings the wooden elements are exposed in different uses classes: Use class 3 in wood elements above ground and exposed to the weather, where even we can find wood elements in sub-class 3.1(not remain wet for long periods) and sub-class 3.2 (remain wet for long periods), and use class 4 in ground contact.

Natural durability and thermal modification of Pinus radiata

Wood, due to its organic nature, is exposed of the degrading action of biological agents (moulds, wood disfiguring fungi, wood destroying fungi and wood destroying insects) and abiotic agents (mainly atmospheric agents as sun and rain).

Biological agents are responsible for attacks that cause reductions in the resistant of wood elements and consequently their physical and mechanical properties. Abiotic agents themselves do not cause serious damage, however unsuitable environmental conditions allow biological agents attacks and affect the final performance.

The natural durability of a wood species is the inherent resistance to attack by wood destroying organisms. In terms of natural durability, heartwood of *Pinus radiata* is classified in the European Standard EN 350 (European Committee Standardization 2016) as not durable regarding to fungi decay (durability class 4-5) and durable against wood boring beetles (class D), which means that its durability and performance for outdoor purposes, i.e. facades and deckings, is not enough as indicated in EN 460 (European Committee Standardization 1995) and its necessary to enhance it low durability, for example by thermal modification (Herrera 2017).

The first thermal modified plant in Spain, located in Basque country, produces thermal modified products at medium industrial scale under the patent Termogenik, using a Mahild chamber with saturated steam atmosphere as heating medium, and modifying wood at temperatures between 192 and 212 °C. This plant uses mainly *Pinus radiata*, very common in plantations in this region of North of Spain. In the situation cases studied (facades and deckings), the wood used is *Pinus radiata* modified at 212 ºC.

Climatic conditions

Weather conditions are a key consideration in the performance exterior wood elements. Climatic parameters such as: rain, wind or UV radiation strongly affects the durability susceptibility to decays and performance of wood used in exterior conditions.

The high variability of the climate conditions affects the biological hazard to which the wood is exposed in exterior uses. In some countries, as Spain, environmental conditions are certainly variables throughout the year and depending also of geographical location.

In Spain, the following levels of Scheffer Index (Fernández-Golfín *et al*. 2016) have been defined as one of the parameters to approach and characterize climatic areas.

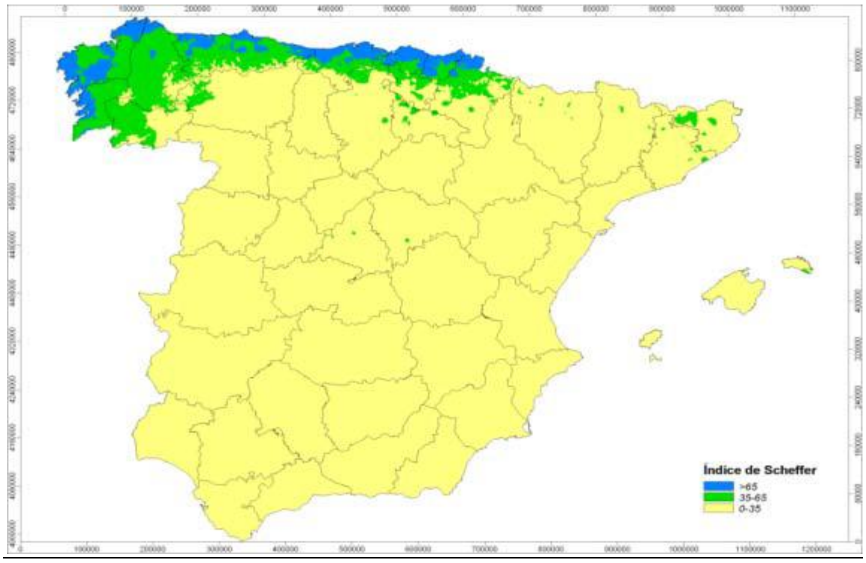


Figure 1: Scheffer index in Spain.

It´s also important to remark the importance of local climates. In some locations, for example high ambient humidity can occur (consequence of water resources such as river banks or oceanic coast or even in areas with frequent fogs), orientations to driven rain, etc., may influence in the final performance of wood.

Design details

Another very important item to ensure a good performance of wooden elements exposed to weathering (in the case of North of Spain, especially to rainfall) is the design details (Davies and Wood 2010).

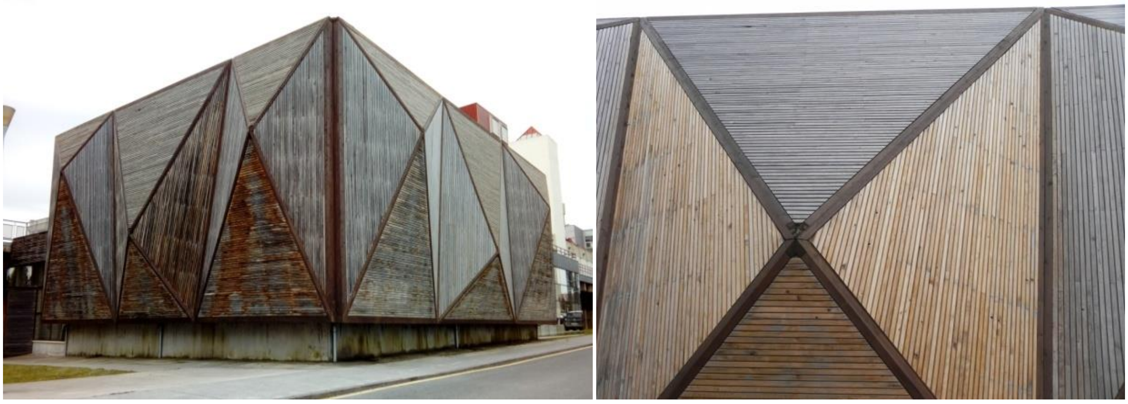
This factor includes design details such as orientation of the fibers, exposure of the end grain, joints, sheltering, distance from ground, etc., which avoids wet conditions in the material and the attack of wood by moulds and fungi, grey sun degradation and general aesthetics problems. So the design must ensure ventilation and rapid evacuation of water in different elements, especially in joints and avoid the water traps.

RESULTS AND DISCUSSION

The real cases of facades and deckings show are located in the North of Spain, a wet and warm climate area. The first example is a Spanish project with thermally modified *Pinus radiata* used in the façade, and decking as friendly building material in a passive house located in Asturias (North Spain) built in 2012. Detail designs were considered (separation between wood elements, sheltering, etc.) and a natural coating was applied. Two years ago, following the maintenance program, the coating was renewed. After six years of exposure in coastal climatic conditions, the thermal modified radiata pine wood elements, installed in the facade and decking, have a very good performance, without discolorations, deformations or cracks.

Figures 2 and 3: Passive house, facade and decking.

The second case is a facade in the University of Basque Country in Bilbao (North Spain) built in 2012. Detail designs were considered, but in this case a coating was not applied. After six years of exposure, there are grey discolorations in the exposed areas of the thermal modified radiata pine facade. All protected parts of the façade, not exposed, have a good performance without discolorations or cracks or stability problems. So, the performance in this case fail due aesthetic aspects.



Figures 4 and 5: Facade of thermal Pinus radiata in the University of Basque Country.

The last example is a thermal modified radiate pine round subproduct from plywood industry, built in 2011 in Orozko (North Spain). The façade is exposed to South-West in a valley with strong driven rain from the South-West. The façade doesn't have coating and there are good design details (as sheltering or separation between round wood) but at the same time there is not distance from ground or some parts of the façade are totally exposed to weathering. After seven years exposure, all exposed parts of the façade are affected by grey discoloration and the areas of the facade near to the ground are splashed and wet; and affected by moulds and wood disfiguring fungi. The performance of the protected areas of the facade is good.

Figures 6 and 7: Different views of the thermal modified round radiata pine in Orozko.

CONCLUSIONS

The use of thermal modified pinus radiata in outdoor elements, as facades and deckings, is a very interesting solution and can provide a good performance in a wet climate as the North of Spain, but if happened if considering a correct thermal treatment process temperature, an adequate design details and applying a coating with a maintenance program, resulting is a good performance if all these factors are considering. But, if the design details are not adequate and if it is not applied a coating, the performance of facades and deckings leaves to the appearance of grey discoloration, moulds and wood disfiguring fungi, with the consequence of aesthetic problems in the thermal wood elements and a no good performance.

In the North of Spain, warm, wet and moderate climate, there are not problems in thermal modified pinus radiata with deformations or cracks in the situation cases studied.

The performance of thermal modified radiata pine elements of facades and deckings with design details and coating is good, without pathological or aesthetics problems and continues to serve their original purpose.

These examples confirm the ability of using thermal modified radiata pine in facades and deckings, in wet and warm climates like North Spain, where wood destroying fungi and other pathological processes can develop and attack the wooden elements during the most of the year.

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Water free PEG impregnation of hardwood veneer using a roll press

Tillmann Meints [1], Axel Rindler [2], Niklas Bugelnig [3]
and Christian Hansmann [4]

[1]Wood K plus - Competence Centre of Wood Composites and Wood Chemistry, Altenberger Strasse 69, 4040 Linz, Austria [t.meints@kplus-wood.at]

[2]Wood K plus - Competence Centre of Wood Composites and Wood Chemistry, Altenberger Strasse 69, 4040 Linz, Austria [a.rindler@kplus-wood.at]

[3]BOKU Vienna - University of Natural Resources and Life Science, Konrad Lorenzstrasse 24, 3430 Tulln, Austria [niklas@bugelnigholz.at]

[4]Wood K plus - Competence Centre of Wood Composites and Wood Chemistry, Altenberger Strasse 69, 4040 Linz, Austria [c.hansmann@kplus-wood.at]

Keywords: impregnation, oak veneer, PEG (polyethylene glycol), roll press, wood modification

ABSTRACT

PEG in wood is usually used to stabilize archaeological waterlogged wooden constructions like the Bremen Cog or the Swedish warship Vasa. However, the superb dimensional stabilizing properties and the non-toxicity of PEG are rarely used in wood industry. The huge drawback of water-based vacuum-pressure-impregnation could overcome by the use of liquid PEG 400 in 100 % concentration in combination with side selective impregnation of oak veneer sheets. The water free continuous impregnation resulted in WPG of 8 % and surprisingly strong deformation, due to veneer-side selective swelling. Veneer thickness, initial wood moisture content and more process parameter were varied to optimize the process.

INTRODUCTION

Today, the major application of Polyethylene glycol (PEG) in combination with wood, is the stabilisation and preservation of waterlogged, archaeological wood structures. Prominent examples are wooden sailboats like the Swedish “Vasa” of the “Bremen Cog”. The current investigation aims to analyse the potential of this established niche application of PEG for processes in wood industry.

PEG impregnated wood shows significantly increased dimensional stability with changing wood moisture content, compared to untreated wood (Stamm 1956, Jeremic 2007, Meints 2018). The main approach to transport the highly hydrophilic PEG into the wood bulk is done via an aqueous solution. The impregnation conditions vary between long term diffusion concentration-gradient- (Stamm 1956) and short term pressure-gradient approaches (Meints 2018). As a common denominator, after the treatment, there is always a higher water content in the wood then before and it needs to be dried afterwards. For certain applications and products, it is desired to avoid this additional water insertion. Therefore, a new water free approach for the impregnation of wood (veneer) is aimed. As a secondary goal, the impregnation from one side only was aimed, mimicking a bi-layer-like swelling behaviour. A tertiary aim finally was the possibility of a treatment in a continuous production line.

EXPERIMENTAL

For the experiments European Oak veneers in the thickness of 0.9 mm and 1.4 mm were used. Veneer sheets were cut to the size of 300 x 90 mm² (longitudinal x tangential). 70 specimens of each thickness were prepared and dried (48 h / 103 °C) to determine dry weight and then each 35 specimens were conditioned back in standard climate at 20 °C and 65 %relH and 35 specimens were conditioned at 20 °C / 95 %relH. PEG 400 (polyethylene glycol, Sigma-Aldrich, Vienna, Austria) was used as impregnation agent, since it is fluid at room temperature at 100 % concentration. For the treatment a roll-press (Model HVF, Mathis AG, Oberhasli, Swiss) was used, to press the veneers after PEG 400 was applied on one surface. The amount of PEG 400 applied on one surface was varied between 80 g/m² and 120 g/m². The pressing procedure was varied in 1-3 m/min speed and 1-6 bar system pressure. The weight gain (WPG, weight percent gain, Eqn: 1) was determined after pressing.

$$\text{WPG (\%)} = ((M_1 - M_2)/M_1) \times 100 \qquad (1)$$

Another output value was the deformation, expressed in tangential bending, measured as highest points from plane surface (“lift”) by laser (Fig. 3). All experiments were planned and evaluated using Design-Expert software (Stat-Ease, Inc., Minneapolis, US).

Figure 1: Roll pressing of an oak veneer sheet, coated with PEG 400. Excessive PEG (~ 50 %) dropping down.

RESULTS AND DISCUSSION

Roughly 50 % of the applied PEG 400 retained in/on the veneer after pressing (compare Fig. 1). The experiments resulted in PEG loadings of 8 % WPG in average. However, the loss in PEG is uncritical, since it can be easily recycled. The amount of WPG is mainly dependent on veneer thickness and the initial wood moisture content. Thinner veneers took up substantially more PEG in relation to the initial weight of untreated veneers (Fig. 2). Regarding moisture content, the veneers conditioned to ~12 % wood moisture content were able to achieve slightly higher WPG values, compared to specimen conditioned to ~24 % wood moisture content (Fig. 2). The treatment factors PEG application amount, treatment pressure and treatment speed had only minor influence on WPG.

Since the PEG was applied on one side of the veneer sheets only, PEG did not diffuse homogeneously through the entire cross-section. That resulted in a bending of the sheets in radial direction for up to 180°, due to swelling of the impregnated side of the sheets (Fig. 3). The swelling took around 2 weeks in standard climate (20 °C / 65 %relH) to reach equilibrium state. Thin veneers were much more prone to deformation (19.6 mm mean lift) than thicker ones (9.0 mm mean lift). That is caused by higher WPG and therefore higher swelling of the thin veneers due to PEG on the one hand and on the other hand by the lower stiffness of the thinner veneer in general.

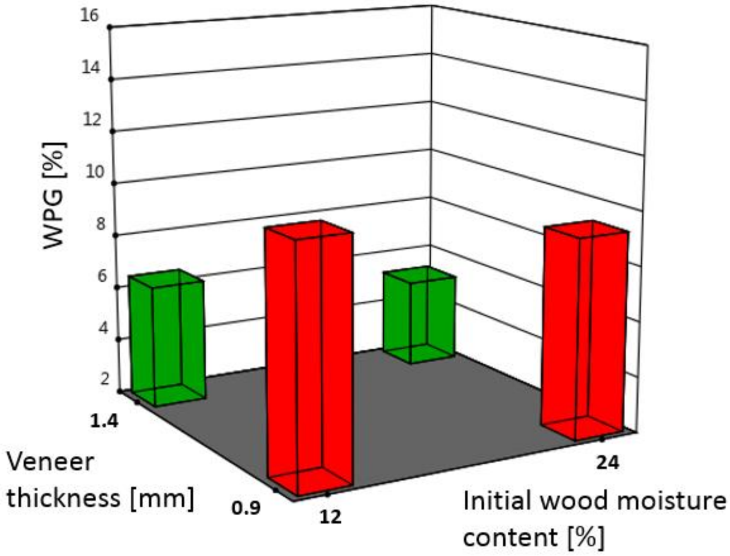

Figure 2: Resulting WPG depending on veneer thickness and initial wood moisture content. Output from Design-Expert software.

Figure 3: Deformation of oak veneer, 1 week after treatment. Upper side treated with PEG 400. Red dot indicates laser aided deformation measuring. Green arrow: lift distance as deformation indicator.

CONCLUSIONS

The carried out investigation showed:

- It is possible to impregnate fluid substances (PEG 400) into wood veneer in a continuous pressing process in 100 % concentration – without the addition of water as solvent.
- WPG loadings of >10 % were achieved and no drying step is necessary.
- It is possible to treat only one side / surface, to generate different properties within one layer, resulting in bi-layer-like deformation.
- Side selective treatment resulted in deformation of up to 180°, which opens interesting new perspectives in fields, dominated by classical bi-layer solutions.

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The impact of cerium dioxide nanoparticles on thermally modified wood-coating system during weathering

Josip Miklečić[1] and Vlatka Jirouš-Rajković[2]

[1] Faculty of Forestry, University of Zagreb, Svetosimunska 25, 10000 Zagreb, Croatia
[email: jmiklecic@sumfak.hr]
[2] Faculty of Forestry, University of Zagreb, Svetosimunska 25, 10000 Zagreb, Croatia
[email: vjirous@sumfak.hr]

Keywords: cerium dioxide, nanoparticles, thermally modified wood, weathering

ABSTRACT

The development of clear coatings with minimal use of harmful chemical to extend the lifetime of wood and maintain its natural look has become very important. However, the clear coatings transmit harmful solar radiation, which causes degradation of wood surface. To increase the coating and wood durability and retain transparency of coating, nanosized inorganic UV absorbers are increasingly used. In this research the samples of unmodified and thermally modified ash wood (*Fraxinus excelsior* L.) finished with nanoparticles-modified waterborne stain were studied. The samples were coated with commercial clear waterborne stain in which the CeO_2 nanoparticles were added in three concentrations (1, 2 and 3%). Coated and uncoated wood samples were exposed for six weeks to UV-light and high moisture in QUV tester equipped with UVA-340 fluorescent lamps. During artificial weathering change in colour and gloss was measured and after artificial weathering the change in water permeability was evaluated. The results of colour change (ΔE^*) of unmodified and thermally modified ash wood samples showed that CeO_2 nanoparticles had a greater impact on colour stability of thermally modified wood than on unmodified wood after artificial weathering.

INTRODUCTION

From previous research, it is known that the thermally modified wood (TMW) loses dark colour when it is exposed to sunlight and therefore it is necessary to protect TMW with coatings. The development of clear coatings with minimal use of a harmful chemical to extend the lifetime of wood and maintain its natural look has become very important. The main problem in selecting of a coating is to determine the balance between preserving the natural look of wood and protection of wood surface and recently between increasingly stringent environmental regulations (Saha *et al.* 2011). Therefore, the use of waterborne clear coatings tends to increase. However, the clear coatings transmit harmful solar radiation, which causes degradation of wood surface (Feist and Hon 1984, Deka and Petrič 2008). To increase the coating and wood durability and retain transparency of coating, nanosized inorganic UV absorbers are increasingly used. Nikolic *et al.* (2015) reported that inorganic nanoparticles can be efficient UV absorbers in coatings depending on the type, loading, size and dispersion of the nanoparticles.

The aim of this research was to investigate the impact of cerium dioxide (CeO_2) nanoparticles on colour and gloss stability and water permeability of coated thermally modified wood after artificial weathering.

EXPERIMENTAL

Wood samples

In this research radial-textured samples of unmodified and thermally modified ash wood (*Fraxinus excelsior* L.) clear and without any visible defects were used. Wood samples were thermally modified at 190 °C used ThermoWood® process (Finish Thermowood Association). Before applying the coatings, wood samples were hand-sanded with paper grit size 120. The samples were coated with commercial clear waterborne stain in which the CeO_2 nanoparticles were added in three concentrations (1, 2 and 3 %). All coatings were applied in two layers in the amount of (120±12) g/m^2 per layer with a 24-hour drying time between layers, which gave the dry film thickness of (68±5) µm.

Artificial weathering

Coated and uncoated wood samples were exposed for six weeks to UV-light and high moisture in QUV tester equipped with UVA-340 fluorescent lamps. The parameters of one cycle were as follows: total duration 168 h (1 week), fourteen intervals comprising 4 h condensation at (45 ± 3) °C plus 8 h UV lamps at (60 ± 3) °C black panel temperature and 0.77 W/m^2nm radiation. Wood samples were exposed to UV light directly at the distance of 50 mm. The ends of wood samples were sealed with two coats of two-component epoxide coating to avoid extensive end-grain water uptake.

Colour and gloss change and water permeability

Colour measurements were performed with a portable spectrophotometer (d/8° measuring geometry, 10° standard observer, D65 standard illuminate, aperture 10 mm) on 8 locations per sample. The overall colour change ΔE* was measured using the CIE L*a*b* colour measuring system according to HRN EN ISO 11664-4 (2014).

Gloss changes were measured with a portable gloss-meter at the angle of 60° on three locations per sample, in a direction parallel to the wood grain.

After artificial weathering, water permeability was measured on three exposed and three unexposed samples for each type of coating. The sides, and-grains and reverse faces of samples were coated with two layers of epoxy coating. The face of samples was placed down on the surface of the water for 72 h and the water uptake in grams was calculated.

RESULTS AND DISCUSSION

Colour changes of uncoated (N) and coated samples after artificial and natural weathering are presented in Figure 1. It can be seen that the addition of nano CeO_2 in the net coating resulted in a greater colour stability of TMW than of unmodified wood. However, the increase of nanoparticle concentration from 1 to 3 % did not result in pronounced reduction in colour change. Also, it can be seen that the colour change of TMW samples was smaller than colour change of unmodified wood samples after artificial weathering.

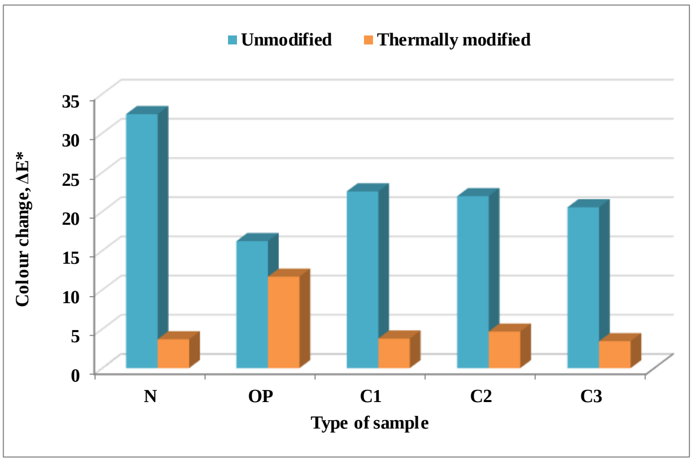

Figure 1: Colour change of uncoated and coated unmodified and thermally modified wood samples (N-uncoated samples, OP-samples coated with neat coating, C1, C2 and C3-samples coated with neat coating + 1, 2 and 3 % of nano CeO_2)

The artificial weathering on all samples caused the reduction of gloss (Figure 2) which could be related with photodegradation of coated wood surface (Cristea *et al.* 2010) and appearance of microroughness. Furthermore, it can be seen that nano CeO_2 had no particular influence on gloss stability of TMW and unmodified wood samples after artificial weathering and that the gloss change was considerably higher on coated samples than on uncoated samples.

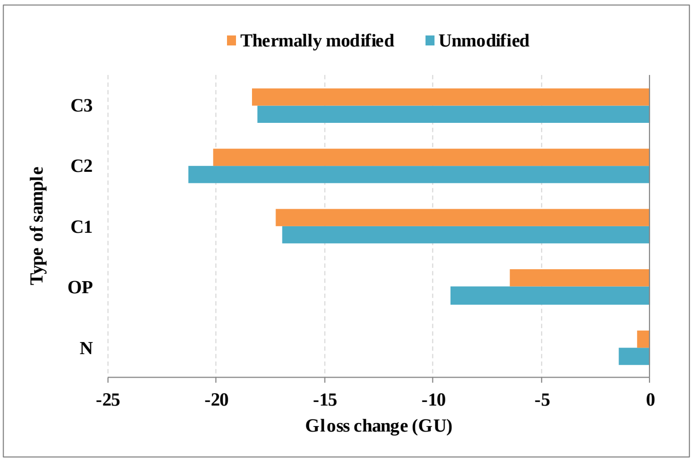

Figure 2: Gloss change of uncoated and coated unmodified and thermally modified wood samples (N-uncoated samples, OP-samples coated with neat coating, C1, C2 and C3-samples coated with neat coating + 1, 2 and 3 % of nano CeO_2)

The results of water permeability show that TMW had lower water permeability than unmodified wood, which has already been confirmed in many studies. Furthermore, it can be concluded that water permeability of coated samples was more related to the type of substrate than the type of coating (Figure 3). Adding of nano CeO_2 into the net coating slightly decreased water permeability of TMW and unmodified wood samples. Moreover, permeability was basically retained at the same level after accelerated weathering, except for the C3-QUV coating on unmodified sample where it increased due to the formation of surface cracks.

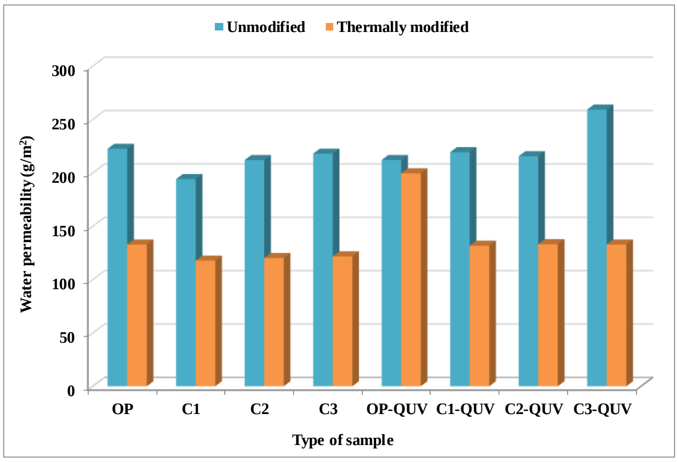

Figure 3: Water permeability of coated unmodified and thermally modified wood samples before and after artificial weathering (N-uncoated samples, OP-samples coated with neat coating, C1, C2 and C3-samples coated with neat coating + 1, 2 and 3 % of nano CeO_2)

CONCLUSIONS

In this research, it was established that CeO_2 nanoparticles had a greater impact on colour stability of thermally modified wood than on unmodified wood and they had a very small influence on gloss stability of coated samples after artificial weathering. Also, it can be concluded that the water permeability of coated samples was more related to the type of substrate than the type of coating.

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Application of time-temperature-humidity superposition to the hygrothermally accelerated ageing of spruce wood

Eiichi Obataya[1], Nanami Zeniya[1], Kaoru Endo[1] and Miyuki Matsuo-Ueda[2]

[1]Graduate School of Life and Environmental Sciences, Tsukuba University, Tsukuba 305-8572, Japan
[email: obataya.eiichi.fu@u.tsukuba.ac.jp]
[2]Graduate School of Bioagricultural Sciences, Nagoya University, Nagoya 464-8601, Japan
[email: miyuki@agr.nagoya-u.ac.jp]

Keywords: Ageing, thermal treatment, time-temperature-humidity superposition

ABSTRACT

Sitka spruce wood specimens were treated at different temperatures (*T*, 95–140°C) and relative humidities (RHh, 0–92%). The plots of mass loss (ML) *vs.* time (*t*) were successfully superposed into a single master curve using shift factors a_T and a_H representing the effects of *T* and RHh, respectively. The *t*–*T*–RHh superposition allowed us to predict the ML and ML–dependent physical properties of wood at arbitrary *T* and RHh. The specific dynamic Young's modulus (E'/ρ) and mechanical loss tangent (tan δ) were predicted to remain almost unchanged by ageing at 20°C and 0–80% RH, whereas those values of naturally aged wood were scattered. In contrast, the predicted CIELAB color parameters reasonably agreed with those of naturally aged wood. The hygrothermal treatment is a useful option to predict the effects of long-term ageing in ambient conditions, particularly when the target property depends simply on the chemical changes in wood constituents.

INTRODUCTION

Hygrothermal treatment is sometimes regarded as a method of accelerated ageing because chemical reactions involved in natural ageing can be accelerated by elevating temperature. Since the acoustic quality of wood is thought to be improved by long-term natural ageing, accelerated ageing has been of interest to artisans making wooden musical instruments. Artificially aged wood is also a useful material for the restoration of old wooden cultural properties.

For precise reproduction of aged wood by hygrothermal treatment, we need to clarify the effects of relative humidity during heating (RHh), because natural ageing proceeds at ambient temperatures and moderate relative humidity (RH). However, industrial hygrothermal treatments are usually conducted in the absence of moisture (0% RHh) or in saturated water vapor (100% RHh), and only a few investigations have focused on the effects of heating at the intermediate RHh (Borrega and Kärenlampi 2007, 2008). In addition, little information is available for the vibrational or dynamic viscoelastic properties of hygrothermally treated wood, whereas its mechanical (static) properties have been investigated well.

We have recently proposed a time (*t*)–RHh superposition to evaluate the mass loss (ML) due to heating at 120°C and different RHh (Endo et al. 2016). In the present study, that method was expanded to wider *T* range (95–140°C) to predict the ML of wood at arbitrary *T* and RHh. In addition, we attempted to predict the physical properties of wood at 20°C, by combining the *t*–*T*–RHh superposition and ML dependencies of experimentally determined physical properties.

EXPERIMENTAL

Wood specimens

A Sitka spruce wood (*Picea sitchensis*) selected for harp soundboard was cut into strips with dimensions of 1.6 mm (tangential) × 15 mm (radial) × 120 mm (longitudinal) and used in this study. The average air-dry density of the specimens was 438 kg/m^3.

Vibration test

The specific dynamic Young's modulus (E'/ρ) and mechanical loss tangent ($\tan\delta$) of the wood specimens were determined at 25°C and 60% RH by the free–free flexural vibration method. The E'/ρ was calculated from the resonance frequency of the first mode vibration, and $\tan\delta$ was determined by approximation of the resonance curve with a theoretical equation.

Color measurement

The CIELAB color parameters (*L**, *a**, *b**) of the edge-grain surface of the wood specimens were measured with a spectrophotometer (UV-3100PC, Shimadzu Co.) using a D65 light source and an observation angle of 10°. Five specimens were tested for each treatment condition, and measurements were obtained at three locations in each specimen.

Hygrothermal treatment

Wood specimens were hygrothermally treated at 120°C and 140°C for 1 – 7 days in an autoclave used in a previous study (Endo et al. 2016). The wood specimens previously conditioned at different values of RH were placed in the autoclave with a certain amount of water depending on the expected RHh, and then the autoclave was tightly closed and heated to expected temperatures. For heating at 95°C, a temperature humidity-controlled chamber (PHP-2J, ESPEC Co.) was used. For heating at 140°C and 0% RHh, a part of the specimens were heated in an oven for 12 – 47 days to achieve sufficient ML values comparable to those achieved by heating in moist conditions. Eight specimens were used for each treatment condition. After the heat treatments, the specimens were immediately cooled to room temperature, and vacuum-dried on P_2O_5 to determine their absolute dry mass. The ML is defined by

$$\mathrm{ML}\ (\%) = 100 \times (M_u - M_t)/M_u \qquad (1)$$

where M_u and M_t are the absolute dry masses of unmodified and hygrothermally treated wood specimens, respectively.

Moistening treatment

Hygrothermal treatment involves temporary, reversible changes in physical properties due to the physical rearrangement (physical ageing) of wood polymers (Obataya 2010, Endo et al. 2016). To eliminate the reversible effect, Wentzel et al. (2018) recently proposed repeated water soaking. However, water soaking does not only remove the reversible effect but also induces *irreversible* loss of water soluble decomposition residues which have a significant impact on the vibrational properties of wood. To prevent any misunderstanding, here we define the *reversible* effect of hygrothermal treatment as *temporary changes in physical properties of wood due to hygrothermal treatment, which are recoverable by moistening at room temperature and 100% RH, without any irreversible loss of wood constituents*. Based on this definition, wood specimens were moistened at 25°C and 100% RH for more than 1 month prior to the measurements of equilibrium moisture content (EMC), vibrational properties and color.

RESULTS AND DISCUSSION

Figure 1a exhibits the ML due to hygrothermal treatment at 62% RH as a function of *t*. Higher *T* resulted in greater ML. By using a shift factor a_T, the plots of ML *vs.* *t* were successfully superposed into a single master curve at 120°C as shown in Figure 1b.

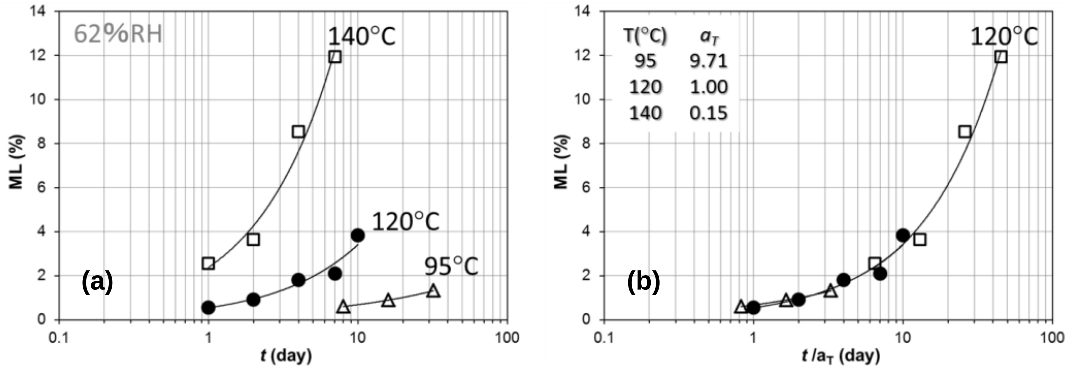

Figure 1: ML due to hygrothermal treatment at different temperatures (T) and 62% RHh as a function of t (a) and the results of t–T superposition using a shift factor a_T (b)

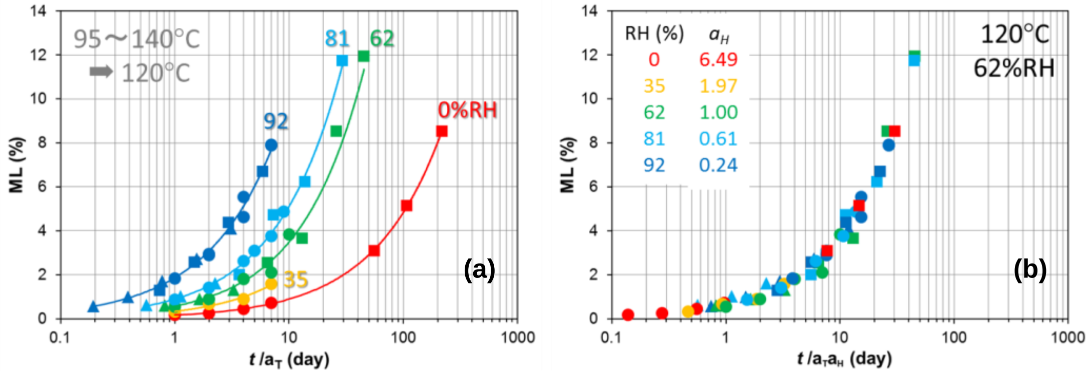

Figure 2: ML due to hygrothermal treatment at 120 ℃ and the indicated relative humidities (RHh) as a function of t/a_T (a) and the results of t–RHh superposition using a shift factor a_H (b)

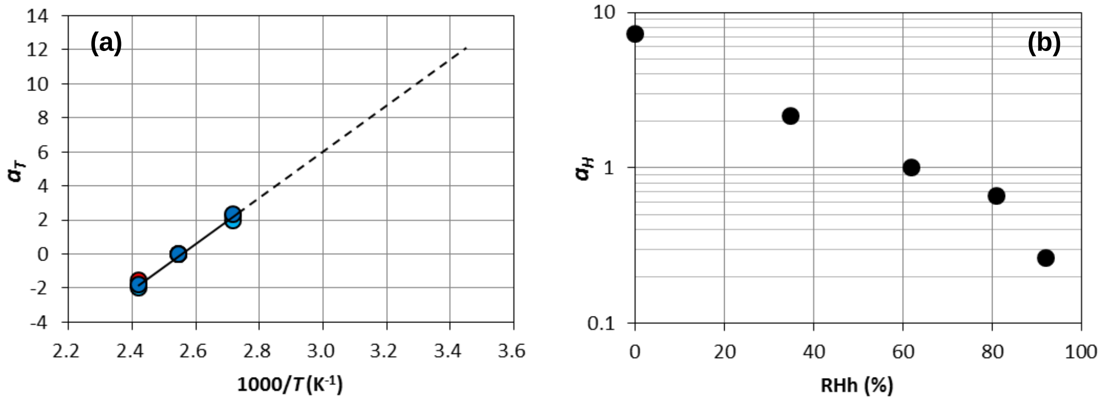

Figure 3: Plots of a_T vs. reciprocal of heating temperature (a) and those of a_H vs. RHh (b). Different point colors indicate different RHh exhibited in Figure 2.

In the same manner described above, different master curves at different RHh (Figure 2a) were superposed into a single master curve, using a shift factor a_H (Figure 2b).
Figure 3a and 3b show the effects of T and RHh on the shift factors a_T and a_H, respectively. The a_T slightly depended on RHh, but such RHh dependency was negligibly smaller than that of a_H. That is, a_T and a_H can be independently determined by T and RHh, respectively. Those factors enable us to predict the ML at arbitrary T and RHh.

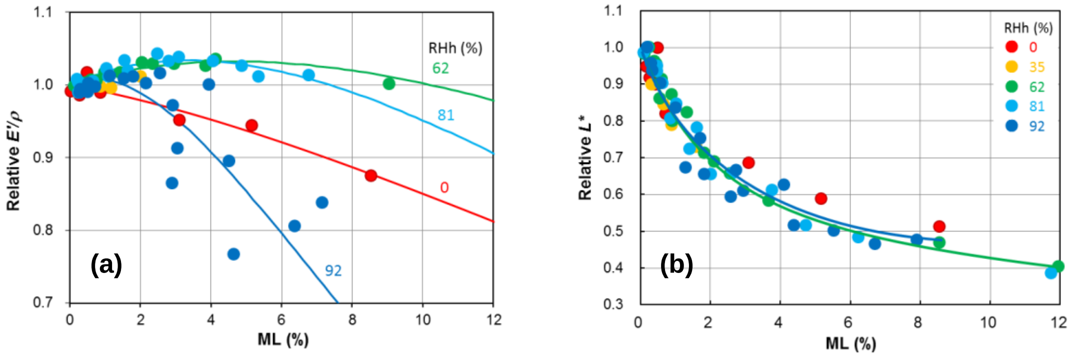

Figure 4: ML dependency of E'/ρ (a) and that of L^* (b) for wood hygrothermally treated at 95-140℃ and RHh indicated.

Figures 4a and 4b show the relative E'/ρ and L^* values of hygrothermally treated wood as a function of ML, respectively. To eliminate natural variations in the physical properties of unmodified wood, the E'/ρ and L^* values of hygrothermally treated wood were divided by those of the wood in the unmodified state. At the same ML, the mechanical properties such as E'/ρ varied depending on the RHh, whereas color parameters depended simply on ML regardless of RHh. Those physical parameters were approximated by the following empirical equation:

$$y = 1 + p_1[1 - \exp(-\mathrm{ML}/q_1)] - p_2[1 - \exp(-\mathrm{ML}/q_2)] \qquad (2)$$

where y is the relative value of any physical property. When T, RHh and ML are known, we can estimate the physical properties of hygrothermally treated wood by using Eqn.2.

Finally, the changes in wood properties at 20°C were predicted by combining t–T–RHh superposition and ML dependencies of physical properties, as exhibited in Figure 5. The E'/ρ value was predicted to remain almost unchanged or slightly increased by ageing at 0–80% *RH*, whereas it decreases with the elapse of time at 95% RH. This suggests the excellent durability of wood in dry condition. In Figure 4, the E'/ρ values of naturally aged wood (Yokoyama *et al.* 2009) are also exhibited. The plots of naturally aged wood are widely scattered compared to the predicted results, probably because the effect of ageing is masked by the original variation in the naturally aged wood samples. In contrast, the predicted L^* values showed reasonable agreement with those of naturally aged wood (Matsuo et al. 2011), because the color of wood reflects chemical changes in wood polymers and is independent of anatomical or structural factors such as microfibril angle. These facts suggest that hygrothermal treatment and t–T–RHh superposition are useful options to predict the effects of long-term ageing in ambient conditions, particularly when the target property depends simply on the chemical changes in wood constituents.

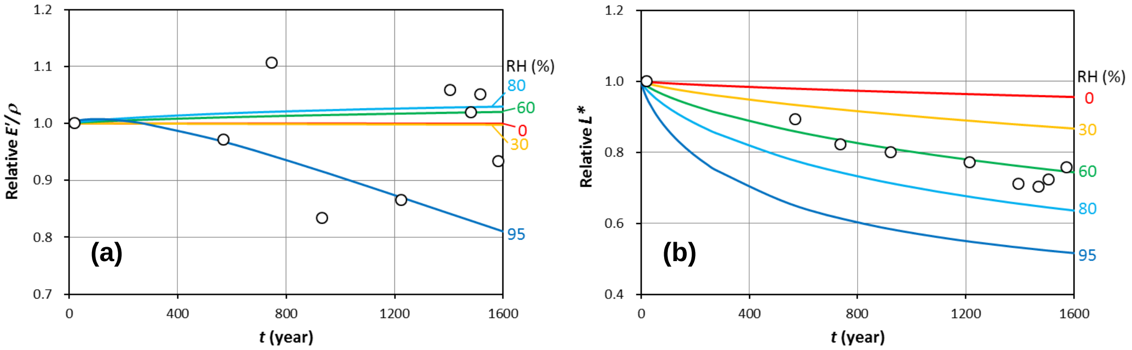

Figure 5: Predicted changes in E'/ρ (a) and L^* (b) at 20 ℃ and different RHs with the elapse of time. Circles represent experimental values of aged cypress wood (Yokoyama et al. 2009, Matsuo et al. 2011).

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Preliminary studies on the effect of acetylation and subsequent weathering on tensile strength and stiffness of Rubber wood (*Hevea brasiliensis*)

S.O. Olaniran[1], E. Cabane[1,2], M. Rüggeberg[1,2]

[1]Institute for Building Materials, ETH Zürich, 8093 Zürich, Switzerland
[2]Laboratory of Applied Wood Materials, Empa, 8600 Dübendorf, Switzerland
[e-mail: olsamuel@ethz.ch; cabanee@ethz.ch; mrueggeberg@ethz.ch]

Keywords: Acetylation, Elastic modulus, Rubber wood, Tensile strength, Weathering

ABSTRACT

The over-exploitation of durable hardwoods has led to the necessity of utilization of other, so far less used species, in Nigeria. One of these species is rubber wood. However, rubber wood is dimensionally unstable in the presence of moisture and subject to degradation by biotic and abiotic agents. To enhance dimensional stability and service life, we have chosen the chemical modification technique acetylation, because its process is established and commercialized. In this preliminary study, rubber wood was harvested from a private rubber plantation in Nigeria. Acetylation was conducted at 70°C for 8 hours and 48 hours achieving a weight percent gain of around 6% and 10% respectively. As a novelty, acetylated rubber wood samples were mechanically characterized by tensile tests prior to and after two weeks of accelerated weathering. In the preliminary results reported here, no significant difference in tensile strength was observed for non-modified and acetylated rubber wood, whereas there was a significant reduction in stiffness due to acetylation. After two weeks of weathering, the tensile strength of non-modified rubber wood was reduced by around 70%, whereas the reduction was less pronounced for the acetylated samples. While a significant decrease in stiffness was observed for the unmodified rubber wood, the acetylated rubber wood retained its stiffness during weathering.

INTRODUCTION

Rubber wood is increasingly utilized as an alternative source of timber in Nigeria. Rubber trees were previously considered as agricultural products and as a source for latex production for rubber and tyre industries. Rubber wood is less dimensional stable in the presence of moisture and less durable in terms of resistance to degradation by biotic and abiotic agents, which currently limits its use as a high value timber species.

Acetylation of wood is a well-established process, and its efficiency in enhancing the dimensional stability of wood has been proven multiple times (Ramsden *et al.* 1997, Hill *et al.* 2006). Resistance of acetylated wood to bio-deteriorating agents has also been reported by various authors for termites, fungi and bacteria (Tillman 1987, Mohebby and Militz 2010, Gascón-Garrido *et al.* 2013). Other studies reported the prevention of photo-discolouration by acetylation and the improvement of lignin stability during weathering (Evans *et al.* 2000, Pu and Ragaukas 2005). Thus, research on acetylation has primarily addressed the benefits regarding dimensional stability and durability.

However, it is also important to take into consideration the influence of the modification on the mechanical properties of wood. Previous studies on the influence of acetylation on the mechanical properties of wood have reported some changes (Evans *et al.* 2000, Larson-Brelid *et al.* 2000, Rowell 2012). Yet, more details are required for the mechanical behaviour of acetylated wood subjected to weathering as there are still debates on the effect of degradation of wood polymers on the mechanical properties of wood during weathering process. A previous report has shown that there is no mechanical loss due to weathering (Colom *et al.* 2003) without adequate information to back up this claim.

In the present preliminary study, we have analysed the effect of acetylation and weathering on the mechanical stiffness and strength of Rubber wood. Investigating the mechanical properties of acetylated rubber wood will help to take advantage of the commercial treatment of acetylation for use in the building sectors in Nigeria.

EXPERIMENTAL

One rubber tree was harvested from a private plantation in the south-western region of Nigeria and processed into boards of 500 mm × 120mm × 40 mm. The tree age was well over 30 years and the tree had been previously tapped for latex. The boards were selected one metre away from the buttress up to one metre above breast height (bh). Samples of 50 mm ×15 mm ×1 mm size were prepared from the boards and grouped into four batches: reference un-weathered, acetylated un-weathered, reference and acetylated with two weeks of weathering. Each batch contained five samples. For acetylation, rubber wood samples were oven-dried at 65°C for 48 hours until constant weight was attained. Acetylation process started with impregnation of the wood samples in the mixture of Dimethylformamide (DMF) and acetic anhydride (50v/v%) for 18 hours. The mixture was thereafter heated up to 70°C under reflux for 8 or 48 hours. Afterwards the acetylated samples were washed in acetone for five days to remove excess acetic acid, and then oven-dried at 65°C for 48 hours. The weight percent gain (WPG) of the acetylated rubber wood was calculated from the dry mass of wood before modification (Mu), and the dry mass of the modified wood (Mm) as shown in equation 1.

$$\mathrm{WPG}\ (\%) = [(M_m - M_u)/M_u] \times 100 \qquad (1)$$

Reference and acetylated samples were subjected to two weeks of weathering. For this, samples were conditioned at 65% RH prior to accelerated weathering in the QUV Accelerated weathering chamber (Q-Lab, Miami, USA). The exposure time was two weeks and weathering protocol was standardized according to EN 927-6, and customised with the use of alternate cycles of UV exposure and water spray. For the analysis of mechanical properties, all samples were cut to a dumbbell shape and tested in tension in fibre direction using the Zwick/Roell Universal testing machine equipped with 10 kN load cell at a test speed of 1mm/min. Strain measurement was enabled by video extensiometry. With the corresponding stress values, the elastic modulus was calculated. For tensile strength, only the samples that failed outside the grip were selected.

RESULTS AND DISCUSSION

By the acetylation of Rubber wood, a WPG of around 6% and 10% was obtained (Figure 1a). This WPG is comparable of those achieved in previous studies on acetylation of rubber wood. A value of 10-16% seems to be the maximum possible WPG obtained so far with temperatures above 100°C and very long treatment times (Pandey and Pitman 2002; Rafidah *et al.* 2006; Pandey and Srinivas 2015). The equilibrium moisture content (EMC) at 65% RH decreased from around 10 % for un-modified rubber wood, and in the range of 4.3 to 6% for acetylated rubber wood at WPGs of 10% and 6% respectively (Figure 1b). Similar EMC was obtained for rubber wood by Chauhan *et al.* (2001) with acetylation of rubber wood to an average WPG of 13.8%. The visual inspection of the weathered samples showed some cracks and distortions in the reference samples and a slight colour change (Figure 1c). The acetylated samples do not show any cracks, neither distortions, and the colour has become lighter compared to that of the reference samples. This colour change is quite characteristic of acetylated wood exposed to solar radiation (Ayadi *et al.* 2003). The effect of acetylation on elastic modulus is shown in Figure 2a. In the un-weathered samples, elastic modulus was significantly reduced by an average of 18% due to acetylation.

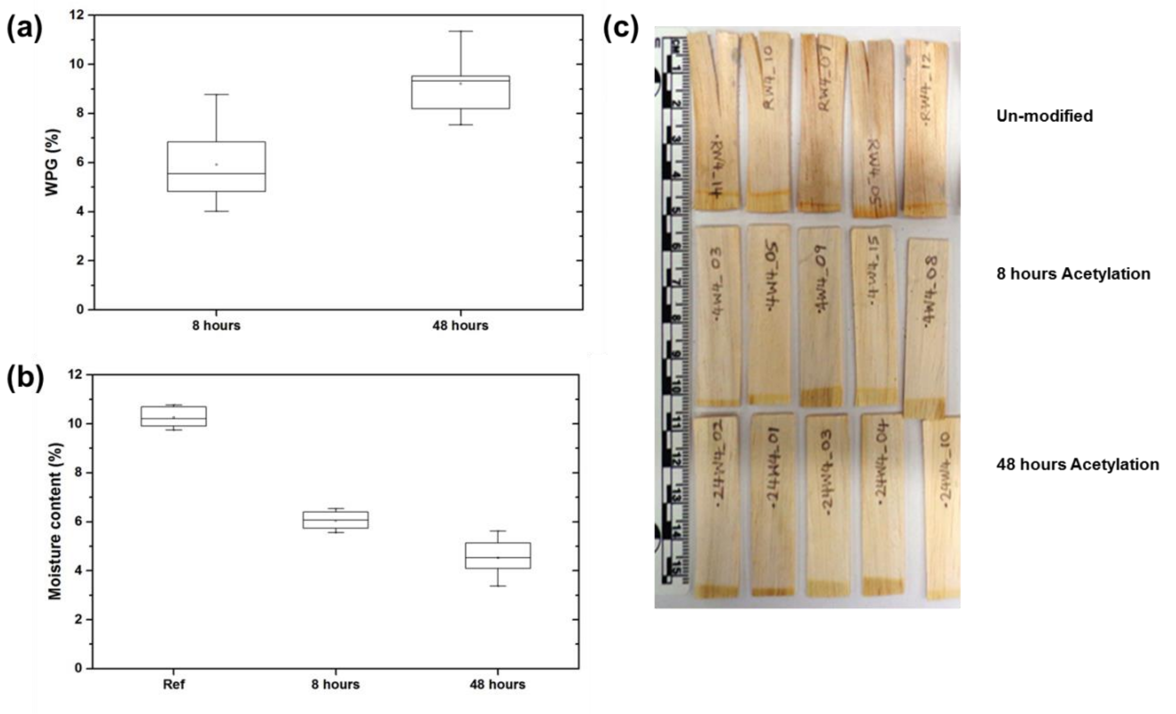

Figure 1. (a). Weight percent gain and (b). equilibrium moisture content (at 65% RH) of acetylated Rubber wood. (c).Visual appearance of weathered Rubber wood at two weeks (336 hours), showing cracks in the reference samples and no cracks in acetylated samples.

After weathering, elastic modulus in the un-modified samples significantly decreased by 13%. On the other hand, the acetylated samples retained their stiffness after weathering. Acetylation had no significant effect on tensile strength, but a significant decrease in tensile strength is observed for reference and acetylated samples after weathering. Reference samples showed a reduction of around 70% (Figure 2b), whereas the tensile strength of acetylated samples is reduced by around 35%.

The retention of stiffness and the reduced loss in strength of acetylated samples after weathering may be attributed to a protection of cellulose against degradation in the acetylated samples, in contrast to the reduced stiffness and the pronounced decrease in strength of the reference samples, which may be caused by a degradation of cellulose due to weathering. According to Evans *et al.* (2000), Derbyshire and Miller (1981), acetylation to low WPGs has often led to increase in susceptibility of cellulose to degradation, a process that commences first by matrix degradation. For higher WPG, however, the susceptibility of cellulose to degradation is reduced according to these studies. It seems that the WPG obtained in the present study may be high enough for protecting cellulose from degradation. This would be in line with the generally lower maximum WPG gain achievable for rubber wood with a rather high density compared to other species (e.g. Obataya *et al.* 2003. for spruce with over 20% WPG).

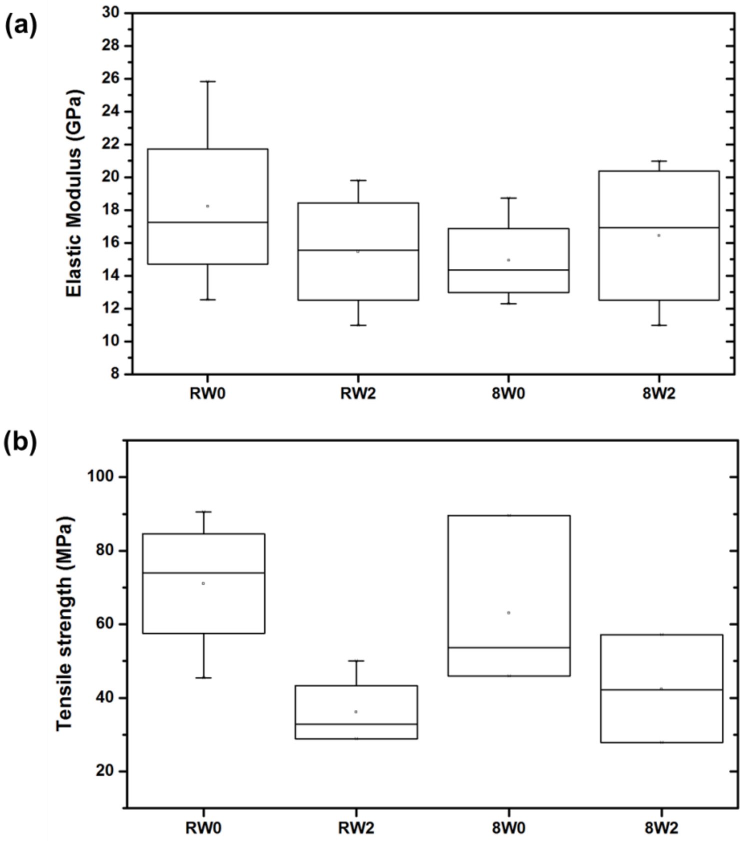

Figure 2. (a). Elastic modulus and (b). tensile strength for the un-modified and acetylated Rubber wood before and after weathering at two weeks of weathering.

CONCLUSIONS

This preliminary study has shown that acetylation is quite effective in preventing loss of stiffness and strength during weathering of Rubber wood. More investigation is required to characterize the weathered samples chemically for correlating the mechanical behaviour to change in the structure and chemistry of the wood cell wall. This will further enhance our understanding of the protective mechanisms of acetylation and on the particular benefits for Rubber wood.

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Mild torrefaction pre-treatment of eucalypts aiming at its energetic valorisation

Solange de Oliveira Araújo,[1] Duarte M. Neiva,[2,] Angélica de Cássia Carneiro[3], Bruno Esteves[4] Jorge Gominho[5] and Helena Pereira[6]

[1]Centro de Estudos Florestais, Instituto Superior de Agronomia, Universidade de Lisboa, Tapada da Ajuda, 1349-017 Lisboa, Portugal [email: araujo@isa.ulisboa.pt)]
[2]Centro de Estudos Florestais, Instituto Superior de Agronomia, Universidade de Lisboa, Tapada da Ajuda, 1349-017 Lisboa, Portugal [email: duarte.neiva@isa.ulisboa.pt)]
[3]Universidade Federal de Viçosa (UFV), Avenida Peter Henry Rolfs s/n, 36571-000 - Viçosa, Minas Gerais, Brazil [cassiacarneiro1@gmail.com)]
[4]Polytechnic Institute of Viseu, Centre for the Study of Education, Technologies and Health (CI&DETS), Portugal; [bruno@demad.estv.ipv.pt)]
[5]Centro de Estudos Florestais, Instituto Superior de Agronomia, Universidade de Lisboa, Tapada da Ajuda, 1349-017 Lisboa, Portugal [email: jgominho@isa.ulisboa.pt)]
[6]Centro de Estudos Florestais, Instituto Superior de Agronomia, Universidade de Lisboa, Tapada da Ajuda, 1349-017 Lisboa, Portugal [email: hpereira@isa.ulisboa.pt)]

Keywords: Elemental composition, Eucalyptus, High heating value (HHV), Thermogravimetric analysis (TGA), Torrefaction

ABSTRACT

Torrefaction is a promising pre-treatment for improving the fuel quality of biomass. This study examined the effect of a mild torrefaction (from 160 to 230 ºC) on the heating value, elemental composition, and thermogravimetric analysis of wood from eight *Eucalyptus* species (*E. botryoides*, *E. globulus*, *E. grandis*, *E. maculata*, *E. propinqua*, *E. rudis*, *E. saligna*, and *E. viminalis*). The higher heating values (HHV) increased from the initial average of 19 MJ kg^{-1} to 21 MJ kg^{-1} in the torrefied samples. The carbon content increased from 48.2% to 53.3% and the C/O ratio from 1.08 to 1.35. The torrefied wood samples showed more thermal stability with a shift of the mass loss peaks to higher temperatures and a higher residual mass at 450 ºC of 36%, in comparison to 30% for the untreated samples. Torrefaction concentrated the biomass samples in the more energetic and thermal resistant components and decreased their sulfur and chlorine content, leading to a better combustion performance. The wood of the eight *Eucalyptus* species had a similar behaviour and showed quality improvement. The mild torrefaction showed potential as a pre-treatment for eucalyptus biomass fuel improvement.

INTRODUCTION

Energy is a requirement in our everyday life as a way of improving human development leading to economic growth and productivity. Climate change is a pressing matter nowadays, leading to the search of new and better non-fossil fuel energy sources to help mitigate this problem and in a sustainable way providing future generations their energy needs (Owusu and Asumadu–Sarkodie, 2016).Sustainable development has become the center of recent national policies, strategies and development plans of many countries (Lu et al 2015).

Biomass accounts for the largest fraction worldwide among the different renewable energy sources, and although its use is still low compared with other sources (IEA 2012) the number of rural communities relying on the traditional use of biomass is projected to rise from 2.7 billion today to 2.8 billion in 2030 (Kaygusuz, 2012).

Biomass may be used to meet a variety of energy needs, including electricity, home heating, vehicle fueling, and industrial process heating. The wood industries and homeowners are the major consumers of biomass energy, *e.g.*, timber, pulp and paper industries burn their own wood wastes to supply approximately 60% of their energy needs (Balat and Ayar 2005).

However, the use of wood biomass for energy production has some limitations, mostly due to its physical properties. In general, raw biomass is characterized by a high moisture content, hygroscopic behavior, low energy density (the primary energy conversion technologies only reach 15% to 20% conversion efficiency), low density and storage problems. Furthermore, the costs of transportation for this material over long distances makes it economically unfeasible (Chen *et al.* 2007).

Torrefaction of biomass is a process that addresses some of the downsides of the lignocellulose material for energy production. This thermal modification process is used to improve the wood quality being especially targeted to: increase durability; improve dimensional stability; decrease equilibrium moisture content; reduce oxygen-rich volatile compounds with low calorific value (resulting in a reduction in hydroxyl groups) (Esteves and Pereira 2009). Thermal modification is performed by heating the wood at temperatures between 180 and 260 °C, usually in the absence of oxygen or under air deficiency (Homan, 2004), leading to a more homogeneous material with higher energy density, while maintaining in average 90% of the energy and 70% of the mass content in relation to the raw material (Rodrigues 2009).

This work studied the effect of a mild torrefaction treatment on the wood of eight eucalyptus species (*E. botryoides*, *E. globulus*, *E. grandis*, *E. maculata*, *E. propinqua*, *E. rudis*, *E. saligna*, and *E. viminalis*). Both raw wood and torrefied products were characterized by thermogravimetric analysis, higher heating value (HHV), and elemental composition to determine the influence of this treatment aiming at a better material for energy production.

EXPERIMENTAL

Six-year-old trees from eight eucalyptus species (*Eucalyptus botryoides*, *E. globulus*, *E. grandis*, *E. maculata, E. propinqua, E. rudis*, *E. saligna*, and *E. viminalis*) were collected in the fields of the School of Agriculture (ISA), University of Lisbon (ULisboa), Lisbon, Portugal. The lower stem logs from the base to 1.3 m of height were sawn into boards with dimensions 60 x 7.5 x 2 cm^3 (in axial, tangential, and radial directions). These boards were torrefied with gradual heating from 160 to 230 °C by the Portuguese company Santos & Santos Madeiras (S&S) under the registered trademark Atlanticwood, a thermo-modification process.

The higher heating value (HHV) was determined using an Adiabatic Bomb Calorimeter. For this analysis, the samples were oven-dried at 103 °C ± 2 °C until a constant mass was reached. The elemental composition was determined with a Perkin-Elmer ll 2400 element analyzer. The composition regarding carbon, nitrogen, and hydrogen (CHN) was determined, as well as Ca, Cl and S, while the oxygen concentration was calculated as (100-(ash + carbon + hydrogen + sulfur + nitrogen)) difference.

Thermogravimetric analysis (TGA) and derivative thermogravimetry (DTG) measurements were carried out using a Shimadzu DTG-60H in a dynamic nitrogen atmosphere (gas flow of 50 mL min^{-1}) with a temperature range of 10 to 900 °C using a 10 °C/min^{-1} heating rate, using 2 mg ± 0.1 mg samples in a platinum container. The thermogravimetric curve (TG) and the curve of the first derivative of the mass loss (DTG) were recorded. From the TG curves, the mass loss was calculated in the following temperature ranges: 50 to 100 °C, 100 to 150 °C, 150 to 200 °C, 200 to 250 °C, 250 to 300 °C, 300 to 350 °C, 350 to 400 °C, and 400 to 450 °C. The residual mass at 450 °C was also calculated.

RESULTS AND DISCUSSION

The higher heating values of the untreated and torrefied wood samples of the different eucalyptus species are compiled in Table 1.

Table 1. Higher Heating Value (HHV, MJ kg^{-1}) of Untreated and Torrefied Wood Samples from Eight Eucalyptus Species.

Species	HHV (MJ kg^{-1})	
	Untreated	Torrefied
E. botryoides	19.2	21.0
E. globulus	19.0	20.1
E. grandis	19.0	20.9
E. maculata	19.1	19.5
E. propinqua	19.9	21.3
E. rudis	19.2	21.3
E. saligna	19.6	21.0
E. viminalis	19.4	20.8

The calorific values found in this work for the untreated eucalyptus woods fall within literature values, as reported for *E. globulus* (17.6 to 19.8 MJ kg^{-1}), *E. botryoides* (19.9 MJ kg^{-1}), *E. grandis* (18.8 to 19.9 MJ kg^{-1}), *E. maculata* (18.8 to 19.6 MJ kg^{-1}), and *E. saligna* (18 to 19.5 MJ kg^{-1}) (Quirino *et al.* 2005).

The torrefaction increased the calorific values of the wood samples between 2 and 11%, in most of the cases to around 21MJ kg^{-1}. (Table 1). This effect is in accordance with previous reports *e.g.*, the heating value increased from 19 MJ kg^{-1} to 21 or 23 MJ kg^{-1} in torrefied woods (Ciolkosz and Wallace 2011). In eucalyptus wood treated at 220 °C, 250 °C, and 280 °C, the increase was 4%, 10%, and 16%, respectively (Rodrigues 2009).

The results of the elemental analysis are presented in Table 2. There was a clear effect of the torrefaction in the elemental analysis for the eight eucalyptus woods, which presented a similar trend of an increase in carbon and a decrease in oxygen along with a slight decrease in hydrogen with heating.

The higher energy content in the torrefied wood samples was related to the chemical changes that occurred during the heat treatment, mostly derived from the elimination of low energy compounds (Brito et al. 2008). In fact, the torrefied wood samples increased their C content and decreased their O content, resulting in increases of the C/O between 12 to 39%, from an average of 1.1 to 1.4. This was reported for several cases with a higher C content increase for the more severe torrefaction conditions (Bridgeman 2008; Nhuchhen et al. 2014). For eucalyptus wood, 24% more C content and 26% less O content were found after torrefaction at 280 °C for 3 h (Arias 2008).

This C/O increase was related mostly to the degradation of hemicelluloses during the torrefaction process, while lignin (the component with the highest C/O ratio) remained mostly unaltered (Demirbas et al. 2009).

Table 2. Elemental Analysis of Untreated (U) and Torrefied (T) Wood Samples of Eight Eucalyptus Species

Wood		Ash (%)	C (%)	H (%)	N (%)	O (%)	Ca (%)	S (%)	Cl (%)	C/O ratio
E. botryoides	U	0.7	48.27	6.06	0.4	44.10	0.02	0.04	0.4	1,1
	T	1.0	55.33	5.88	0.4	37.11	0.05	0.03	0.3	1,5
E. globulus	U	0.6	48.74	6.12	0.2	43.72	0.07	0.01	0.3	1,1
	T	0.7	51.50	5.77	0.3	41.40	0.10	0.01	0.2	1,2
E. grandis	U	0.6	48.08	6.12	0.2	44.40	0.04	0.01	0.1	1,1
	T	0.6	53.72	5.83	0.2	39.06	0.06	0.01	0.3	1,4
E. maculata	U	1.1	47.55	6.15	0.2	44.78	0.28	0.03	0.2	1,1
	T	1.4	52.67	5.56	0.2	40.31	0.30	0.01	0.1	1,3
E. propinqua	U	0.5	49.17	6.07	0.2	43.38	0.02	0.01	0.3	1,1
	T	0.8	53.75	5.81	0.2	39.08	0.03	0.01	0.2	1,4
E. rudis	U	0.8	46.04	5.70	0.2	46.83	0.04	0.04	0.4	1,0
	T	1.0	53.51	5.74	0.4	39.02	0.09	0.05	0.2	1,4
E. saligna	U	0.4	49.57	6.15	0.2	42.80	0.05	0.01	0.3	1,2
	T	0.6	53.56	5.80	0.2	39.26	0.07	0.01	0.3	1,4
E. viminalis	U	0.7	47.95	6.01	0.2	44.59	0.06	0.01	0.3	1,1
	T	0.7	52.60	5.76	0.2	40.32	0.07	0.01	0.2	1,3

Moreover, the thermal behavior of wood during heating (Fig. 1) showed a first mass loss at the lower-temperature range (the first peak of the DTG curve), which corresponded to the decomposition of the hemicellulose fraction. As the temperature rose, the chemical reactions became more complex and cellulose degradation occurred near 350 °C (the second peak of the DTG curve). Similar results were obtained from the TGA analysis of other kinds of biomass (Hossain 2009; Saddawi *et al.* 2012).

The carbon increase was related mostly to the degradation of hemicelluloses during the torrefaction process, while lignin (the component with the highest carbon content) remained mostly unaltered (Demirbas *et al.* 2009). Moreover, the thermal behavior of wood during heating (Fig. 1) showed a first mass loss at the lower-temperature range (the first peak of the DTG curve), which corresponded to the decomposition of the hemicellulose fraction. As the temperature rose, the chemical reactions became more complex and cellulose degradation occurred near 350 °C (the second peak of the DTG curve). Similar results were obtained from the TGA analysis of other kinds of biomass (Hossain 2009; Saddawi *et al.* 2012; Sen *et al.* 2012).

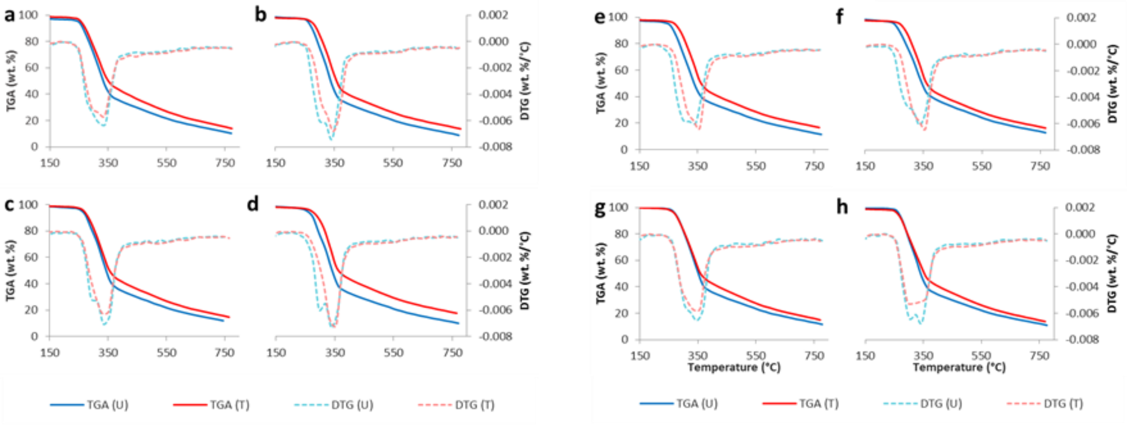

Fig. 1. TGA (left y-axis) and DTG (right y-axis) curves of untreated (U) and heat-treated (T) wood samples of E. botryoides (a), E. globulus (b), E. grandis (c), E. maculata (d), E. propinqua (e), E rudis (f), E. saligna (g) and E. viminalis (h) under a nitrogen atmosphere and 10 °C/min heating rate.

CONCLUSIONS

The mild torrefaction used in this study confirmed an improvement in the biofuel properties of all the tested eucalyptus species, with *E. botryoides*, *E. grandis* and *E rudis* having the highest increases in HHV and C/O ratios. On the other hand *E. maculata* showed very low increase in HHV and *E. globulus* in C/O ratio.

Therefore, the torrefied woods of the different eucalyptus species may be considered a rather homogeneous biofuel. All of the heat-treated wood samples had calorific values higher than the minimum value required by ISO 17225-1.

The wood of the eight *Eucalyptus* species showed different behavior and quality improvement regarding torrefaction, which must be taken into consideration if the raw material is intended for energy production. Nevertheless, the mild torrefaction showed its potential as a pre-treatment for biomass fuel improvement.

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Influence of various polyethylene glycol treatments on the dimensional stability of beech wood

Sabrina Puttmann, Lukas Müller, Bertil Burian and Marcus Müller

Hochschule Rottenburg, Schadenweilerhof, D-72127 Rottenburg am Neckar,

[email: puttmann@hs-rottenburg.de; mueller@hs-rottenburg.de]

Keywords: Beech wood, cross laminated timber, dimensional stability, polyethylene glycol (PEG), wood modification

ABSTRACT

The aim of this study is to improve the dimensional stability of beech wood using wood modification with polyethylene glycol (PEG). The use of different molecular sizes from PEG 400 up to PEG 8000 with three different concentrations is described. The results reveal that the wood can be impregnated with the different molecular sizes of PEG. Both, weight percent gain and bulking were increased by the PEG treatment. Also the dimensional stability was improved. Depending on the used molecular size of PEG and the used concentration, Anti-Swell-Efficiency (ASE) values up to 85 % can be reached.

The idea is to use dimensionally stabilized beech wood for the production of cross-laminated timber (CLT). This enables a constructive use of beech wood in interior areas.

INTRODUCTION

During the last decades, near-natural forestry had a strong impact on wood reserves in German forests. As a result the hardwood amount increased very strongly. Especially the amount of European Beech (*Fagus sylvatica*), as a site-adapted wood species, has got a high share in the German wood reserves (BMEL 2016). Despite the large stocks, beech wood is currently hardly used for constructional applications. This depends on the low dimensional stability of beech wood. In order to increase the amount of hardwood based applications, the dimensional stability has to be improved.

This study is part of a scientific project, which has the aim to use modified beech wood for the production of cross laminated timber (CLT). Up to now CLT is mainly produced of spruce wood. However, due to the changing wood reserves, the use of hardwood species, especially beech wood, for the CLT production has to be developed.

The idea of this study is to improve the dimensional stability of Beech wood by using wood modification with polyethylene glycol (PEG). PEG is a polyether compound, which is used in cosmetic and pharma industries as well for medical applications. In the past, polyethylene glycol has already been studied for the treatment of wood. Areas of application were in particular the conservation of archaeological and marine artefacts, for example the Vasa, a preserved war ship of the 17th century.

Whereas older publications recommend the use of PEG 1000 for industrial applications (Stamm 1964), Jeremic et al. (2007) were able to show that PEG with a molecular size of up to 20000 also penetrate the cell wall of pine wood.

In contrast to common used wood treatments, such as acetylation or thermal modification, PEG leads to no emissions during and after the treatment. In addition no curing of the chemical is needed.

Different molecular sizes from PEG 400 up to PEG 8000 with three different concentrations were used in this study. The main focus is on:

- The influence of the various molecular sizes on the penetration and fixation of beech wood (weight percent gain (WPG), bulking)
- The impact on the dimensional stability of beech wood (ASE)

After successful wood modification, CLT modules will be manufactured from the treated wood. Within the project further investigations, considering mechanical and bonding properties of PEG modified beech wood, will be performed.

EXPERIMENTAL

Material

For the impregnation four different molecular sizes three different concentrations of PEG were used (Table 1).

Table 1: Used PEG molecular sizes and concentrations

Molecular sizes of PEG	**Concentration 1 [%]**	**Concentration 2 [%]**	**Concentration 3 [%]**
PEG 400	10	20	40
PEG 2000	10	20	40
PEG 4000	10	20	40
PEG 8000	10	20	40

Beech wood samples with sizes of 25 x 25 x 10 mm³ (radial x tangential x longitudinal) were used for the impregnation.

Methods

The samples were treated with the PEG solutions by using an impregnation plant. The wood samples were penetrated completely with a vacuum step of thirty minutes and a pressure step of two hours. To determine the weight gain and the bulking of each wood sample, the data (weight and dimensions) were recorded before and after the treatment. The following equations were used for the calculation of weight percent gain (WPG) (Eqn. 1) and bulking (Eqn. 2).

$$\text{WPG (\%)} = ((w_t - w_u)/w_u) \times 100 \qquad (1)$$

w_t = weight of treated, dried wood sample [g]
w_u = weight of untreated, dried wood sample [g]

$$\text{Bulking (\%)} = ((a_t - a_u)/a_u) \times 100 \qquad (2)$$

a_t = area of treated, dried wood sample [cm²]
a_u = area of untreated, dried wood sample [cm²]

Treated, as well as untreated, wood samples were stored in water in order to determine the Anti-Swell-Efficiency (ASE). After each water saturation cycle, the weight and the dimensions of each sample were measured again. One water saturation cycle lasts thirty minutes at vacuum and twenty-four hours at normal conditions. The ASE was calculated using following equations (Eqn. 3 and 4).

$$\text{ASE (\%)} = ((s_u - s_t)/s_u) \times 100 \tag{3}$$

s_t = swell rate of treated samples [%]
s_u = swell rate of untreated sample [%]

$$\text{Swell rate (\%)} = ((a_w - a_d)/a_d) \times 100 \tag{4}$$

a_w = area of water saturated samples [cm²]
a_d = area of anhydrous samples [cm²]

RESULTS AND DISCUSSION

The results reveal that beech wood can be impregnated with the different molecular sizes of PEG. Both the solution uptake and the weight percent gain were increased by the PEG treatment. The weight gain is approximately equal to the used PEG concentration and is not depending on the used molecular sizes of PEG (Figure 1).

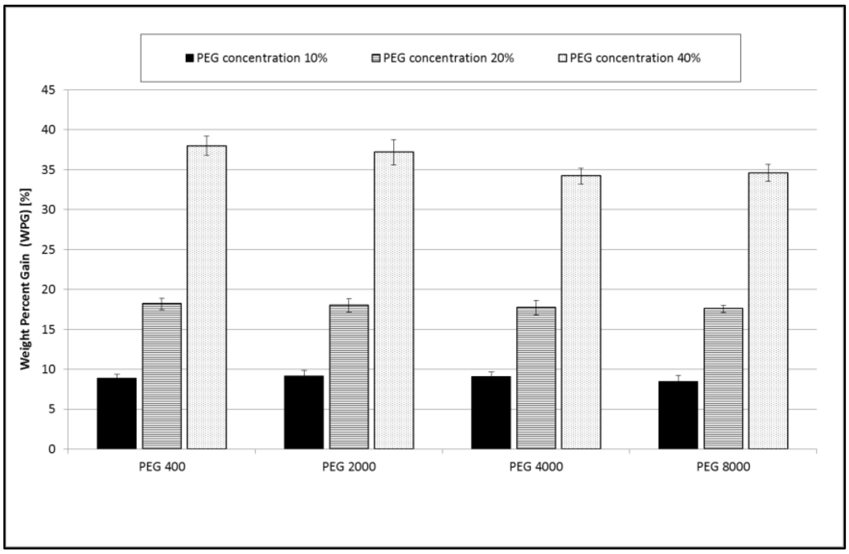

Figure 1: WPG of PEG treated beech wood. Wood treated with three different concentrations (10 %, 20 %, and 40 %) and four different molecular sizes of PEG (PEG 400, PEG 2000, PEG 4000 and PEG 8000).

Bulking values up to 17 % show (Figure 2), that the PEG penetrates the wooden cell wall. These high bulking values are reached by the 40 % concentration of PEG. This corresponds to the findings of Jeremic et al. (2007). They were able to detect particularly high concentrations of PEG in the middle lamella.

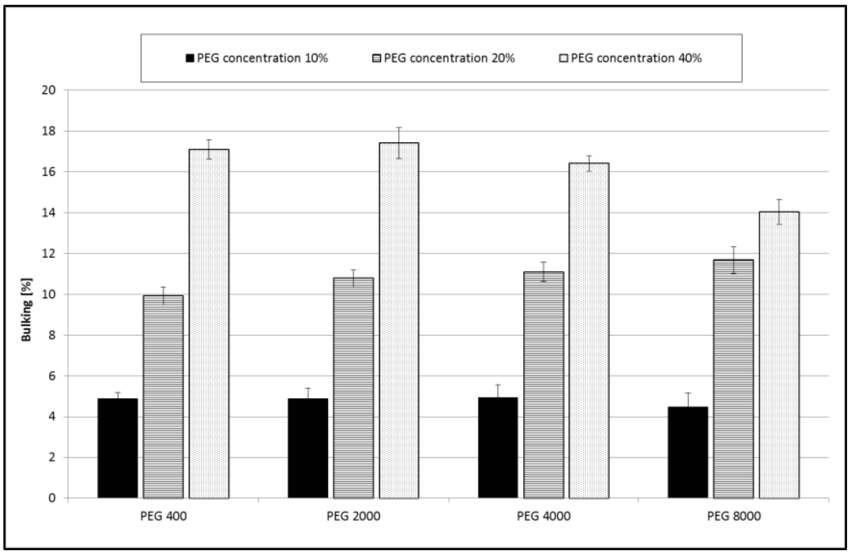

Figure 2: Bulking of PEG treated beech wood. Wood treated with three different concentrations (10 %, 20 %, and 40 %) and four different molecular sizes of PEG (PEG 400, PEG 2000, PEG 4000 and PEG 8000).

The dimensional stability of beech wood can be increased with the PEG as well. Depending on the used concentration of the PEG solution, an Anti-Swell-Efficiency (ASE) up to 85 % can be achieved (Figure 3). Here it is obvious that the PEG 8000 with a concentration of 40 % has a significantly weaker ASE than the PEG variants with smaller molecule sizes. PEG 8000 with higher concentrations seems to penetrate the wood cell walls to a smaller extent. This can also be seen in the bulking results (Figure 2), where the 40 % concentration of PEG 8000 reaches lower values.

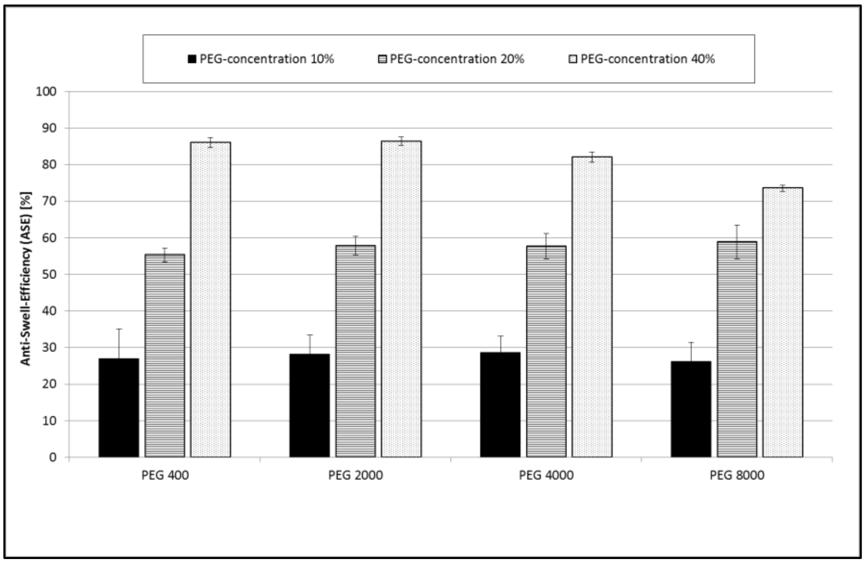

Figure 3: Anti-Swell-Efficiency of PEG treated beech wood after first water leaching. Wood treated with three different concentrations (10 %, 20 %, and 40 %) and four different molecular sizes of PEG (PEG 400, PEG 2000, PEG 4000 and PEG 8000).

Unfortunately, PEG is not sufficiently fixed in the wooden cell wall. It is completely leached out of the wood after three to five water saturations (Figure 4). This corresponds to studies of Bardet et al. (2007), who were able to demonstrate via nuclear magnetic resonance (NMR) that PEG does not form an atomic linkage with the cell wall but reacts with lignin on a molecular level.

However, the larger molecule sizes of PEG showed a delayed leaching effect (Figure 4). PEG 8000 is completely washed out after six water storages, whereas PEG 400 is already completely leached out after three times of water saturations. The molecular size of PEG can slow down the leaching.

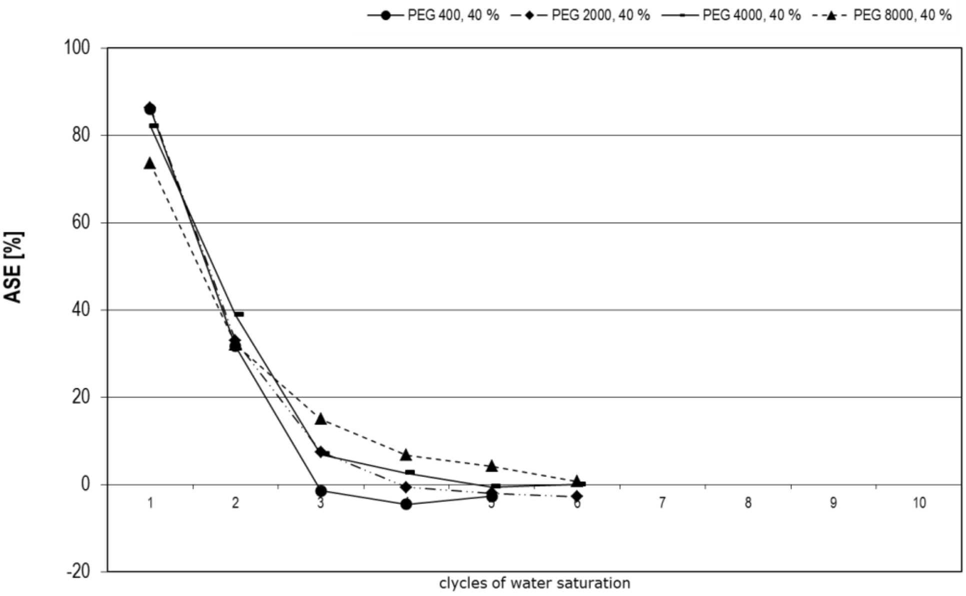

Figure 4: Course of the Anti-Swell-Efficiency (ASE) of PEG treated beech during several water saturations by the example of the PEG concentration of 40 %.

CONCLUSIONS

Due to the high ASE values, the wood modification of beech wood with PEG can be described as very effective. This dimensional stabilization enables the use of PEG modified beech in constructive applications such as CLT. However, the fixation of the PEG in the wood is not permanent. It can be dissolved and washed out again. Therefore, only an interior application is possible.

Further investigations on the topics of mechanical strength and bonding properties are currently in progress. The aim of the research is to develop a CLT prototype made of modified beech wood.

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Adhesion of coatings to plasma modified wood at accelerated weathering

Ladislav Reinprecht[1], Radovan Tiňo[2] and Marek Šomšák[3]

[1]FWST TU, T.G. Masakyka 24, SK-960 53, Zvolen [email: reinprecht@tuzvo.sk]
[2]FCHFT STU, Radlinského 9, SK-812 37, Bratislava [email: radovan.tino@stuba.sk]
[3]Henclová 114, SK-053 33, Nálepkovo [email: mareksomsak@centrum.sk]

Keywords: adhesion, coating, Norway spruce, plasma, weathering

ABSTRACT

Resistance of the coated wood surfaces to weathering is predetermined by more factors, including the interface phase “wood – coating” stability. A better adhesion of coating systems to wood can be increased by its pre-treatment with penetration paints, or in recent years also by its primary surface modification with suitable chemicals, plasma, etc. The goals of plasma use are: (I.) an activation of wood surfaces for adhesion processes, (II.) a better anchoring of coatings into wood surfaces, and (III.) a prolongation of the lifetime of coated wood. The adhesion strength of transparent coatings to Norway spruce (*Picea abies* Karst L.) wood is analyzed in this work, considering following factors: (1) wood surfaces without or with a primary modification by the ADRE “Atmospheric Discharge with Runaway Electrons” low temperature plasma, (2) acrylic or alkyd transparent coatings applied in 3 layers with retention of 115 ± 10 g/m^2 in each layer, (3) coatings containing HALS or BTZ UV-additives in amounts of 0, 0.25, 0.5, or 1 wt. %, and (4) coated wood surfaces without or with 1-week accelerated weathering in Xenotest Q-SUN Xe-1-S by a partly adjusted EN 927-6. The performed experiments have brought these knowledge: (A) the ADRE plasma had a positive effect on the adhesion strength of coatings to wood surfaces, especially of the acrylic one used as a water dispersion; (B) the adhesion strength of acrylic and alkyd coatings to wood surfaces apparently decreased at weathering, whether or not they were plasma-treated; (C) the HALS and BTZ UV-additives did not have any more pronounced (positive or negative) effect on the adhesion strength of coatings to the plasma modified wood, in both cases, without and with accelerated weathering.

INTRODUCTION

In exteriors, due to the sun radiation, rain water, heat, dust, aggressive emissions and other atmospheric factors, the adhesion between coatings and wood surfaces can be more or less impaired. UV radiation penetrates the wood to a depth of approximately 75 micrometers and visible up to a depth of 200-500 micrometers, depending on the density of wood, however, photodegradation of wood occurs also beyond this zone (Kataoka *et al.* 2004, 2007). The coatings usually do not penetrate such depth, which also has a negative effect on the weakening of “wood – coating” stability at weathering processes.

The adhesion strength of coatings to wood affects several factors, in terms of the type of wood, its anatomical and morphological structure as well as its chemical composition including the type and proportion of extracts (Kaygin and Akgun 2008). Several researchers have identified the wood - coating interface as the key parameter to determine the resistance of transparent wood coatings to degradation (Smulski and Côté 1984, Williams *et al.* 1990), as well as their overall stability in the external environment. It is known that the adhesion of the coating system to wood can be increased by its initial treatment with penetration coating, as well as by its pretreatment with suitable chemicals and physical methods (Evans *et al.* 1996), now for example by plasma (Odrašková *et al.* 2008, Viöl 2013). Plasma barrier discharge serves to activate the wood surfaces prior to application of the coating system to ensure its better adhesion to wood. This will also positively affect the life time of treated wood.

EXPERIMENTAL

Wood

The samples with a dimension of 80 mm × 45 mm × 8 mm (longitudinal × radial × tangential) were prepared from Norway spruce (*Picea abies* Karst L.) boards having a moisture content of 12 ± 2%. The top surfaces of boards were grinded gradually with grains with sandpapers with grain size No 60 and No 120. Samples used for experiment did not have biological damages and more apparent growth inhomogeneity.

Plasma modification of wood samples

The modification of top surfaces of spruce samples with a low-temperature plasma was performed in the ADRE (Atmospheric Discharge with Runway Electrons) device. The operating conditions were as follows: 1.4 kW, frequency 2000 Hz, time 60 (Figure 1).

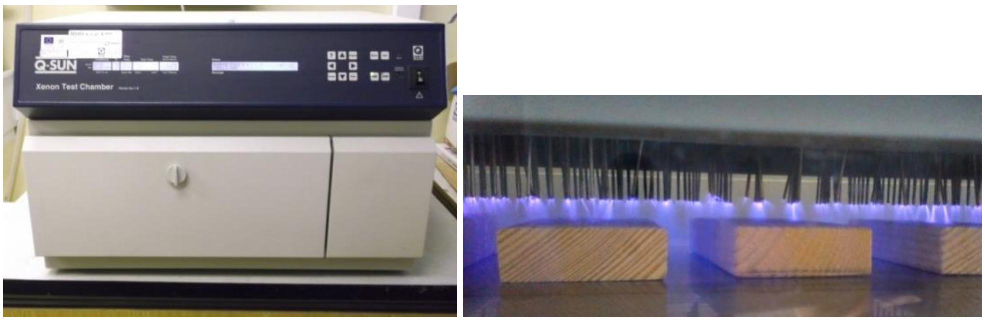

Figure 1: Plasma pre-treatment of the top surfaces of spruce samples in the ADRE device

Coatings and UV-additives

The transparent acrylic (dry mass 28.6%) and alkyd (dry mass 34.9%) coatings were produced in Chemolak Smolenice, Slovakia. Both types of coatings were modified with UV-additives, HALS (Hindered Amine Light Stabilizer) or BTZ (2-(2'-hydroxyphenyl) benzotriazole), in amounts of 0, 0.25, 0.5 and 1 wt. %.

Application of coatings

The application of coatings on the top and all other surfaces of wood samples was performed by pneumatic spraying technology in three layers, each one in quantity 150 ± 10 g per m^2. The other layer was applied after a drying time needed for curing of the previous layer, and after following sanding the layer with sandpaper with grain size No 240.

Accelerated weathering

The 1-week accelerated weathering of coated wood samples was carried out in the Q-SUN Xe-1-S Xenotest (Q-Lab Corporation, USA). The weathering took place according to a modified Standard EN 927-6 (2006), *i.e*. 24 h conditioning of samples at 45°C and then 48 subcycle steps each lasting 3 h (2.5 h UV-radiation and 0.5 h water spraying). Following changes were made to the standard: Xenon lamps instead of fluorescent UV lamps; irradiance at 340 nm set to 0.55 $W \cdot m^{-2} \cdot nm^{-1}$ instead of 0.89 $W \cdot m^{-2}\ nm^{-1}$; temperature on black panel 50°C instead of 60°C.

Adhesion of coatings to wood

The adhesion of coatings to spruce samples was evaluated before and after their accelerated weathering by the tensile strength method perpendicular to the phase interface of the "wood – coating film" system. For the tensile tests was used PosiTest AT-M device (Figure 2) works in accordance with ASTM standards (D4541, D7234), as well with Standard EN ISO 4624 (2016).

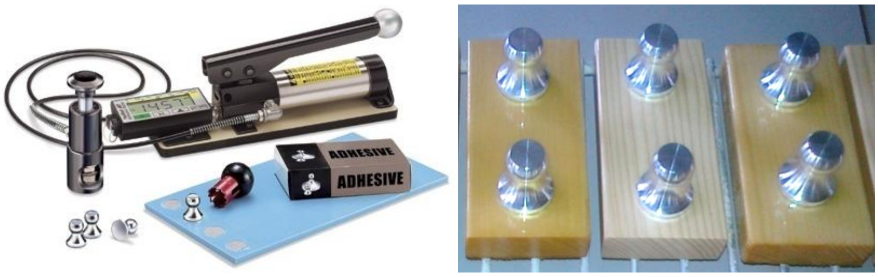

Figure 2: PosiTest AT-M (a) and coated spruce samples with glued rollers (b)

RESULTS AND DISCUSSION

The experimental results are summarized in Tables 1 and 2.

Table 1: Adhesion of acrylic and alkyd coatings to Norway spruce wood – effects of plasma modification of wood surfaces and of accelerated weathering of coated woods in Xenotest

Weathering	**Adhesion [MPa]**			
	Acrylic coating		**Alkyd coating**	
	Native wood	**Plasma wood**	**Native wood**	**Plasma wood**
Without	2.20 (0.5)	2.82 (0.6)	2.58 (0.3)	2.75 (0.3)
1-week in Xenotest	1.79 (0.4)	2.28 (0.5)	2.04 (0.5)	2.27 (0.3)
Percentage drop [%]	18.6	19.2	20.9	17.5

Notes:

- *Mean values are from 16 ($2 \times 2 \times 4$) measurements, i.e. from 2 measurements for each of the defined coating type (acrylic or alkyd), which contained 2 different types of the UV-additives (HALS or BTZ) used in 4 concentrations (0, 0.25, 0.5 or 1 wt. %). This way of evaluation was applied, as effects of the UV-additive type and its concentration in coatings were not important for the adhesion strength (see Table 2).*
- *Standard deviations are in the parentheses.*

The adhesion strength of coatings to the plasma modified spruce samples increased in comparison to the native samples, approximately about 28% at using acrylic coatings and about 6.6% at using alkyd coatings. This tendency was preserved even after accelerated weathering of coated samples (Table 1).

Due to the accelerated weathering the adhesion strength decreased from 17.5% to 20.9%, *i.e.* only with minimal negative or positive effects of the plasma modification of spruce samples and the used coating type (Table 1).

Presence of UV-additives in coatings did not appear to affect their adhesion to spruce samples (Table 2).

Table 2: Unclear impacts of the UV additives (HALS and BTZ) in acrylic and alkyd coatings on the adhesion strength of coatings to spruce samples modified with plasma

UV-additive [wt. %]	**Adhesion [MPa]**			
	Without weathering		**1-week in Xenotest**	
	Acrylic	**Alkyd**	**Acrylic**	**Alkyd**
0	2.85	2.75	2.27	2.31
HALS				
0.25	3.09	2.73	2.59	2.08
0.5	2.92	2.52	2.25	2.20
1.0	2.83	2.70	2.13	2.32
BTZ				
0.25	2.36	3.02	2.17	2.30
0.5	3.06	2.75	2.31	2.41
1.0	2.57	2.77	2.24	2.27

Note:

- *Mean values are from 2 measurements at using the UV-additives in coatings, or from 4 measurements without using the UV-additives in coatings (0 wt. %).*

CONCLUSIONS

On the basis of achieved results the following conclusions were stated:

- the plasma discharge had a positive effect on the adhesion strength of coatings to wood surfaces, especially of the acryl one used as a water dispersion,
- the accelerated weathering had a negative effect on the adhesion strength of acrylic and alkyd coatings used for treatment of the native wood surfaces as well as of the plasma modified ones,
- the UV-additives (HALS and BTZ) did not have any more pronounced (positive or negative) effect on the adhesion strength of coatings to the plasma modified wood, in both cases, without and with accelerated weathering.

ACKNOWLEDGEMENTS

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Measuring Accessibility of OH groups in Scots Pine with Dynamic Vapour Sorption Apparatus

Tuuli Uimonen[1], Saara Hautamäki[1], Maija Kymäläinen[1] and Lauri Rautkari[1]

[1]Aalto University, P.O Box 16300, FI-00076 Aalto [email: tuuli.uimonen@aalto.fi]

Keywords: Accessibility, Dynamic Vapour Sorption, Scots Pine

ABSTRACT

Lately, OH group accessibility measurements have been gaining popularity in solid wood research mainly due to the availability of the Dynamic Vapour Sorption (DVS) apparatus. In this study, a method to measure accessibility of OH groups from Scots pine (*Pinus sylvestris* L.) with the DVS apparatus was investigated. The study focused on the most essential parts of the measurement since the aim was to find optimal measuring parameters for sample mass and exposure time to D_2O vapour. Four different sample masses were tested in the DVS apparatus measurement with water vapour and the optimal sample mass was then chosen to D_2O vapour exposure analysis. Five different exposure times were investigated against the accessibility results and time consumption was also evaluated. The results indicate that the optimal sample mass is around 20 mg and the sample should be exposed to D_2O vapour for at least 10 hours. However, the results are only indicative due to the lack of repeats.

INTRODUCTION

Accessible hydroxyl groups are believed to be the primary sorption sites in wood for water molecules. Currently, the only method to give an actual value for accessibility of the OH groups is the Dynamic Vapour Sorption (DVS) apparatus. In the DVS, the sample mass is measured before and after exposure to D_2O vapour with a sensitive microbalance. The difference in sample mass can be used as a measure for accessible OH groups, since the exchange of hydrogen by deuterium in accessible OH groups results in a mass increase by ca 1 g/mol per exchanged hydrogen. The difference between hydrogen and deuterium atoms is presented in Figure 1. A large mass increase reveals that the sample has an open structure and that OH groups in the cell wall structure can be reached by water. Therefore, the DVS apparatus has made it easy to measure accessibility from wood and several studies have already been published (Rautkari *et al.* 2013, Kymälainen *et al.* 2015, Popescu *et al.* 2014). Still, achieving comparable and repeatable results is a challenge, because no uniform protocol on the accessibility measurement of OH groups in wood exists.

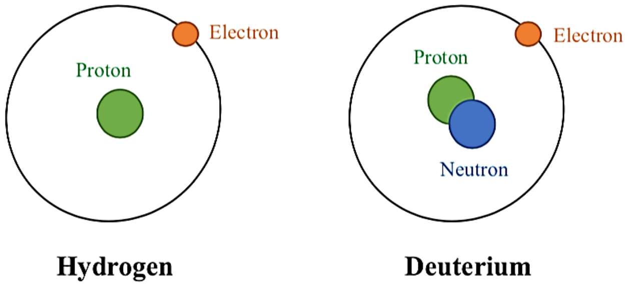

Figure 1: The atomic structure of hydrogen vs. deuterium

Measurement of accessibility with the DVS is affected by several parameters, such as sample mass and step duration as well as the number of steps in the protocol. In literature, sample masses between 5 mg to 20 mg have been reported (Rautkari et al. 2013, Thybring et al. 2017) but no clear reasoning for the chosen masses has been given. The question remains, is a result obtained by using 5 mg samples comparable to results from 20 mg samples. The current paper aims to answer this question, as well as discuss whether the 5 mg sample is suitable for reliable results.

The number of steps in the measurement is mainly depending on the number of rewetting cycles and many papers have been using several cycles (Rautkari *et al.* 2013, Popescu *et al.* 2014). However, it has been proven that the amount of cycles has no effect on the results whereas the total time of D_2O vapour exposure has a significant relevance (Pönni *et al.* 2014). Therefore, only one exposure step is used in this experiment and the focus is rather on the duration of D_2O exposure.

EXPERIMENTAL

Material information

Never-dried board of Finnish Scots pine (*Pinus sylvestris L.*) was used for this study. The board was conditioned at 20°C and 50% RH prior to testing. Samples were cut from the board with razor blade only from the sapwood region.

DVS apparatus

The experiments were carried out with DVS apparatus (DVS Elevated Temperature ET, Surface Measurement Systems Ltd., London, UK) photographed in Figure 2, coupled with liquid ionized water and liquid deuterium oxide (Sigma Aldrich 99,9%). The temperature was kept constant during all the measurements (25°C). Accessibility of OH groups (A) in the sample was calculated with Equation 1.

$$A\ (\text{mol/g}) = (m_D - m_I)/(m_I \times \Delta M) \qquad (1)$$

where m_I is the weight of the sample (g) after first drying step, m_D is the weight of the sample (g) after second drying step. Between the drying steps, the sample has been exposed to D_2O vapour. ΔM is the difference in the atomic mass of hydrogen and deuterium (ΔM = 1.00616 g/mol).

Figure 2: DVS apparatus opened for sample replacement

Sample mass analysis

To assess the optimal sample mass for the DVS measurement for solid wood, four different sample masses were chosen for this experiment. The lowest mass was 5 mg and the greatest 40 mg (Figure 3). Samples were cut in order to keep the early/latewood ratio similar in all the samples. The measurements were done in three steps:

1. First drying step: samples conditioned at 0% RH until mass change rate (dm/dt) was under 0.0005 %/min for 10 minutes.
2. H_2O exposure step: samples conditioned at 95% RH for 24 hours.
3. Second drying step: samples conditioned at 0% RH for 24 hours.

Figure 3: Samples ready for the DVS analysis

D_2O vapour exposure analysis

The optimal time for the exposure of the D_2O vapour was evaluated with one 20 mg sample. Five different times for D_2O vapour exposure were chosen: 2, 6, 10, 14 and 20 hours. The measurements were done in three steps:

1. First drying step: sample conditioned at 0% RH until mass change rate (dm/dt) was under 0.0005 %/min for 10 minutes.
2. D_2O exposure step: sample conditioned at 95% RH for 2-20 hours.
3. Second drying step: samples conditioned at 0% RH until mass change rate (dm/dt) was under 0.0005 %/min for 10 minutes.

The result of the accessibility of OH groups in each measurement was calculated using Eqn. 1.

RESULTS AND DISCUSSION

Analysis of the optimal sample mass

Optimal sample mass was evaluated with four different samples. The last hour of the measurement is illustrated in Figure 4 but the same phenomenon could be seen through the whole measurement. The change in mass (%) is a value calculated from the middle of the last hour (zero-point is when time is 30 minutes) and all the other mass value in the measurement is in relation to the zero-point. Figure 4 shows clearly that with 5 mg sample the oscillation is rather great compared to larger masses. The greater the mass, the smaller the oscillation during the measurement. The reason for oscillation can be argued but one possible explanation could be that temperature and humidity is not totally constant inside the DVS apparatus and they might have an effect on the results. Other explanation might be found from the gas flows inside the machinery, with lighter samples being more sensitive to their effect.

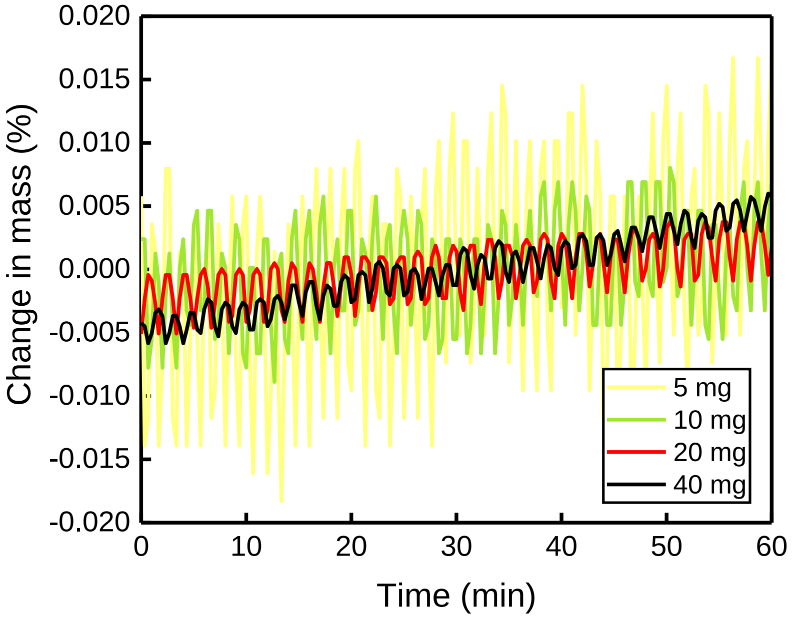

Figure 4: Change in mass (%) when drying the sample. Time zero-point is the beginning of the last hours of 24 hour drying step

In practice, this oscillation means that the mass of the 5 mg sample is constantly changing within ±0.0015 mg whereas in 40 mg sample the change is ±0.0009 mg. The oscillation alone is not that critical for the results since rounding will remove the effect of it in most cases. However, the oscillation has a great effect on the measurement time if the criteria for equilibrium is based on the sample mass change per minute (dm/dt) as seen from Table 1. Typically, accessibility measurements have been done with equilibrium criteria of dm/dt being under 0.002 %/min for 10 minutes (Rautkari *et al.* 2013, Popescu *et al.* 2014) but since that has been recently criticised (Glass et al. 2017), attention should be drawn to lower values of dm/dt. Usually, lower sample masses are used in order to gain time benefit, but Table 1 clearly shows how the benefit is lost when criteria is set lower than 0.002 %/min. Unexpectedly, the best time results are gained with sample mass of 20 mg. Sample masses of 5-10 mg have a greater time since the greater oscillation prevents the sample from reaching the equilibrium criteria fast. Based on these results, sample mass around 20 mg is the optimal sample mass. Besides the time benefit, the higher the sample mass, the more reliable the results will be regarding other matters as well. For example, parameters such as the amount of early and latewood are easier to optimize.

Table 1: Consumption of time to reach a stable mass

Sample mass (mg)	Time (h) for 0.002 %/min	Time (h) for 0.001 %/min	Time (h) for 0.0007 %/min	Time (h) for 0.0005 %/min
5	4.6	9.0	11.6	16.8
10	4.7	8.5	10.3	11.1
20	6.0	8.1	9.8	11.6
40	7.5	10.8	10.8	14.5

Analysis of the optimal exposure time to D_2O vapour

The importance of the exposure time to D_2O vapour was investigated and the aim was to find an optimal parameter to use in the measurements. The results in Figure 5 reveal that time has a quite extreme effect to the results. With a 2-hour exposure, the deuterium exchange is not finalized. Based on the results, it can be argued that the deuterium exchange is still in process also between 6 and 10 hours since the value of accessibility is increasing between them. With 14 hours, the accessibility of OH groups is in the maximum value and, unexpectedly, greater than with 20 hours. Either the result for 14 hours is a measuring mistake or it goes between the standard deviation of the accessibility measurements. However, this experiment do not give an answer to that due to the lack of repeats. To gain more reliable results, this experiment needs to be done again in duplicates or triplicates. However, it can be concluded that the exposure time to D_2O vapour should be over 10 hours to ensure that deuterium exchange is finalized.

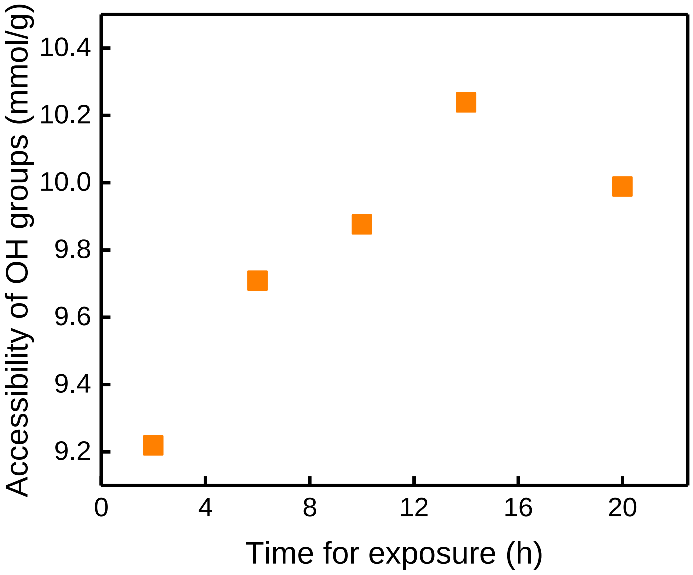

Figure 5: Accessibility results depending on the exposure time

CONCLUSIONS

In this study, a method to measure accessibility of OH groups from Scots pine (*Pinus sylvestris* L.) in the DVS apparatus was investigated. The study focused on the most essential parts of the measurement since the aim was to find optimal measuring parameters for sample mass and exposure time to D_2O vapour. Four different sample masses were tested in the DVS apparatus measurement with water vapour and the optimal sample mass was found to be around 20 mg. The optimal value was found by comparing the oscillation and time dependence of the different masses. The optimal mass was then chosen for D_2O vapour exposure analysis. Five different exposure times were investigated against the accessibility results and time consumption was also evaluated. The results indicate that the sample should be exposed to D_2O vapour for at least 10 hours. However, the results are only indicative and the measurements needs to be done with duplicates or triplicates in order to gain reliable results.

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Plasma treatment of wood veneers: a review

Richard Wascher[1,2], Georg Avramidis[1], Holger Militz[2] and Wolfgang Viöl[1]

[1]University of Applied Sciences and Arts, Faculty of Natural Sciences and Technology, Von-Ossietzky-Strasse 99, 37085 Göttingen, Germany
[2]Wood Biology and Wood Products, Burckhardt-Institute, Georg August University of Göttingen, Büsgenweg 4, 37077 Göttingen, Germany

Keywords: plasma, veneer, liquid uptake, wetting, impregnation, plywood

ABSTRACT

This paper reviews published studies and the author's work in the field of plasma-enhanced modification of wood veneers. The research in this field has demonstrated the effectiveness of a plasma pre-treatment as a prior step of processing wood veneers e.g. with glues or waterborne modification agents such as melamine resins. Wood veneers have been plasma-treated using oxygen-containing process gases at low or atmospheric pressure and subsequently processed to plywood. The investigations have included variations of liquid, wood varieties and plasma-specific settings. In addition, the behaviour of the plywood boards made of plasma-pre-treated veneers has been tested in accordance with common standards for mechanical stresses. The outcome of the experiments clearly indicated an improved wetting and uptake of water and waterborne modification agents. Furthermore, an enhanced dimensional stability of plywood made of plasma pre-treated veneers without compromising mechanical properties could be proved.

INTRODUCTION

Chemical modification of wood often requires the penetration of the modification agents into the core material. Therefore, the raw material usually undergoes a vacuum-pressure process to ensure extensive soaking and distribution of the modification agents within the wooden volume. This is necessary because applying modification agents in conventional immersion processes—even in thin wood veneers—is not efficient due to the slow and insufficient penetration of the reagent into the bulk. However, since vacuum-pressure processes are time and material intensive, plasma pre-treatment represents a method to improve the impregnability of wood veneers for subsequent impregnation steps, enabling the use of simple immersion processes or roller applications. The plasma treatment of wood and wood-based materials represents a relatively new field of research. This type of surface modification involves numerous physical-chemical interactions of plasma-generated species with the wood surface, which may result in cleaning, ablation, and cross-linking effects. Using this method, the substrate can be modified either directly or indirectly. A direct (superficial) modification can be realized by generating protective, hydrophobic layers on the material surface through a plasma polymerization. For this purpose precursors with organic compounds (e.g. siloxane compounds) in the gas phase are commonly used (Zanini 2008; Rowell 2012; Avramidis 2015; Kocaefe 2015). Indirect wood modification can be realized by pre-treatment using a gas discharge operated with oxygen containing gases such as air. In this way the material is provided with hydrophilic properties, for example due to the increase in surface energy, and subsequent processes (*e.g.* impregnation) can be positively influenced (Wolkenhauer 2007a; Riedl 2014). This review addresses the indirect wood modification using plasma processes.

PLASMA

Technically usable plasmas can be generated for example by supplying electrical energy to a gas, which is thereby ionized. Thus, highly reactive radicals, excited molecules and molecular fragments are created. In this state, the gas reacts with the substrate surface in a variety of chemical and physical processes. It is possible to treat the surfaces in a flat, linear, selective or pattern-like way. Furthermore, various approaches exist to produce technical plasmas, ranging from low-pressure discharges excited by microwaves to plasma-jet systems. Figure 1 shows a method for plasma modification of flat (endless) substrates such as veneers; it operates according to the principle of a dielectric barrier discharge (DBD) at atmospheric pressure (Wascher 2016; Wascher 2017a).

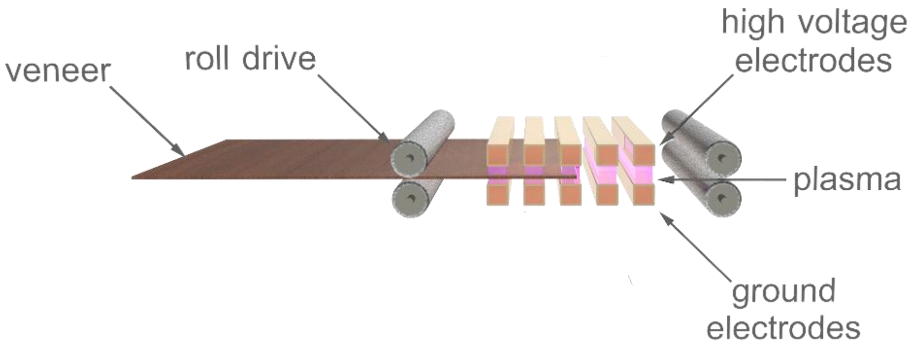

Figure 1: Plasma set-up for veneer pre-treatment (Wascher 2016; Wascher 2017a).

GENERAL EFFECTS ON WOOD AND WOOD-BASED SURFACES INDUCED BY PLASMA TREATMENT

Increased wetting after air plasma treatment is mainly due to the formation of polar groups on the substrate surface (e.g. C=O, O-C-OH), caused by reactions between the substrate surface and the plasma-generated oxygen species (Klarhöfer 2010). A certain increase in surface roughness, which is an already-known effect for plasma modification of polymers (Wolkenhauer 2008), may contribute to improved wettability. Furthermore, exposure to plasma can lead to degradation of wood polymers and accessory materials (Jamali et al. 2011; Avramidis 2012). In addition, the oxygen-containing nitrogen species (NO_x) generated in air plasma (Braun 1988) react with the intrinsic water of the wood to form nitric and nitric acid (Wascher 2014), thus leading to a lowering of the pH on the surface (Odrášková 2008; Peters 2014). Numerous publications have reported improved wetting properties of wood surfaces as a result of plasma treatment of e.g. oak, pine, beech, ash, walnut and maple wood, proved by contact angle (CA) measurements (Topala 2007; Odrášková 2008; Busnel 2010; Lux 2013; Zhang 2015). However, the degree of improvement depends on the type of wood (Avramidis 2010; Busnel 2010) and other factors such as the growth-related areas of wood (early/late wood, sapwood/heartwood) (Vitosytė 2017) or the condition of the wood surface (fresh cut, aged) (Wolkenhauer 2009b).

ACCELERATED LIQUID UPTAKE OF PLASMA-TREATED VENEERS

Especially the plasma treatment of wood veneers has achieved some remarkable results. Yamamoto et al. reported a significant reduction of the water contact angle on spruce and birch veneers (thickness = 0.8 mm) down to 10° (CA untreated: spruce ≈ 120°, birch 140°) after a plasma treatment of 90s duration (Yamamoto 2017). Zhang et al. also demonstrated an improved wetting of the surface of wood veneers (thickness = 0.8 mm) made from *Pinus yunnanensis* after a DBD treatment, whereby a significant reduction of CA in dependence on treatment time (0-260 s) and electrical power (2000-5000 W) could be achieved (Zhang 2015). Aydin and co-workers investigated wetting properties of aged spruce veneer surfaces (9-year storage) after plasma treatment and found that the treatment led to significantly increased wetting with water (Aydin 2010). Using a low-pressure plasma, the wetting of a UF glue on poplar veneer surfaces (thickness = 1.5 mm) as a function of the treatment time (0-540 s) was investigated by Tang et al. (Tang 2012), who found that the CA of UF-glue could be reduced from 40° for the untreated samples to 15° for the plasma-treated samples (treatment time= 540 s). Wolkenhauer et al. demonstrated faster penetration of water and accelerated curing of PVAc-glue for thin (3 mm) air plasma-pretreated particleboards and fiberboards. They attributed this behavior to an accelerated extraction of water from the glue line (Wolkenhauer 2007b; Wolkenhauer 2009a). Avramidis et al. reported analogous results when gluing wood veneers (maple, oak, beech and teak) using PVAc: the curing duration of PVAc on plasma-treated veneers could be halved compared to curing of untreated samples (Avramidis 2011). Investigations on the water absorption of wood veneers (beech, oak, pine and spruce, thickness = 0.6 mm) before and after a plasma treatment (DBD) (Avramidis 2010) showed that the effect of the plasma treatment on improved water or waterborne modification agent (melamine, DMDHEU) uptake depended on the plasma treatment duration, the type of wood and immersion time. The authors attributed this behavior to differences in the anatomical structure as well as in the chemical composition of the different types of wood. Wascher et al. investigated the modification of beech veneers with DMDHEU in dependence of plasma exposure time and duration of impregnation (Wascher 2015). After 120s of plasma treatment, a doubling of the DMDHEU solution uptake compared to the reference could be achieved (immersion duration: 30s). Furthermore, at comparable levels of solution uptake, a 60% increase in bulking was detected. In another study, the effectiveness of a plasma treatment with respect to water uptake was tested on 28 different veneer types (Wascher 2014). 23 out of 28 tested veneers showed a significant improvement in water uptake after plasma treatment — however, at different levels. Four types of veneer showed neither a deterioration nor an improvement; the plasma treatment of spruce veneer led to a significant reduction in water uptake.

Table 1: Examples of the investigations carried out on the plasma treatment of wood veneers (ref = reference, pla = plasma-treated)

wood species	**contact angle [°]**		**water uptake[1] [%]**		**plasma setup**			**research group**
	ref	**pla**	**ref**	**pla**	**source**	**t_{treat} [s]**	**P_{treat} [W]**	
Betula pendula R.	≈115-120	≈10			DBD	90	125	(Yamamoto 2017)
Picea abies L.	≈125-145	≈10						
Pinus yunnanensis	≈100	≈40			DBD	140	4000	(Zhang 2015)
Picea orientalis L.	≈60	≈10			LPP[3]	900	200	(Aydin 2010)
Populus spp.	≈105[2]	≈75			LPP	540	200	(Tang 2012)
Quercus sp.	≈90	<10	≈5	≈9	DBD	10		(Avramidis 2010)
Fagus sylvatica	≈70	<10	≈9	≈22				
Picea abies	≈100	≈40	≈14	≈16				
Pinus sylvestris	≈100	≈60	≈16	≈15				
Fagus sylvatica			≈12	≈22	DBD	5	≈650	(Wascher 2017b)
Fagus sylvatica (therm. mod.)			≈4	≈27				

[1]immersion time: 1s, [2]used liquid: UF-resin, [3]LPP=low pressure plasma.

REASONS OF ACCELERATED LIQUID UPTAKE

The underlying mechanism of improved liquid uptake after plasma treatment of veneers might be related to the complex water supply system of wood. Král et al. (Král 2015) showed by means of XPS on beech wood, that plasma treatment represents a pure surface effect with a limited penetration depth (≈ 300 nm), so that depth effects due to plasma exposition can be ruled out first. However, wood is a porous material and the liquid transport of softwoods takes place via the tracheid system. In addition to tracheids, hardwoods also have other cavity elements, such as the large-lumen vessel elements (Wagenführ 1999; Bosshard 2013). However, these cavities — beside others e.g. production-related microcracks — are the basic prerequisite to create gas discharges within the wood body (more precisely inside the cavity volumes). Another prerequisite for a possible discharge in the cavities is that the wood veneer be located directly between the electrodes. The charge accumulations generated by the gas discharge on the surfaces can induce sufficiently high electric fields directly between the two veneer surfaces (top and bottom of the veneer) to cause electrical breakdown within the cavities. However, the electric field generated between the two veneer surfaces is dependent on the thickness of the substrate, so that the field strength decreases as the substrate thickness increases, possibly explaining why this effect was not observed at larger sample thicknesses. Wascher et al. showed that known effects of air plasma treatment (increase of the oxygen/ carbon ratio, lowering of the pH value, increase of the nitrate concentration, lowering of the contact angle) centrally inside wood veneers (thickness ≈ 1.8 mm) can be explained by the occurrence of a gas discharge within wood cavities during plasma treatment (Wascher 2014). An electrical breakdown within the cavities leads to plasma-modified cavity walls and hence to increased surface energy of the wall surfaces. Since the capillary action is a function of the surface energy, the wood cavities should show enhanced capillary penetration, thus leading to an improved solution uptake of wood veneers when plasma-treated.

FROM VENEERS TO PLYWOOD

An impregnation of wood veneers with modification agents such as melamine resins, DMDHEU or phenolic resins can only be economically reasonable if veneers are further processed to wood materials such as plywood. Plywood made from impregnated veneers generally shows sound mechanical properties. Furthermore, direction-dependent material properties of solid wood, such as swelling and shrinkage behaviour, are minimized for plywood. Due to a sufficiently high degree of loading of the veneers with modification agents, such plywood is suitable for the production of moulded parts and for outdoor use. Thus, in addition to the wetting properties of spruce veneers after a low-pressure plasma treatment, Aydin et al. studied the mechanical properties of plywood (3-ply, glued with UF resin). Due to better wetting and the resulting better bonding quality between single veneer layers of the plywoods made from plasma-treated veneers, the samples exhibited higher strength values than plywood samples produced from aged veneers (Aydin 2010). Temiz et al. investigated the bonding quality of plywood samples made of untreated, copper-based impregnants and compared them with plasma-pretreated (O_2 and N_2 as process gas) beech veneers. Veneers treated with O_2 showed a significantly higher quality of bonding compared to the reference samples (Temiz 2016). Altgen et al. sAvramidis

susceptibility of thermally-modified wood against air plasma exposition compared to unmodified wood (Altgen 2016). Plasma treatment abolishes the hydrophobic properties of thermally-modified wood veneers and significantly enhances uptake of waterborne modifying reagents, thus enabling the production of impregnated plywood from thermally-modified wood veneers for outdoor contexts. The author’s investigations demonstrate that plywood made of thermally-modified and impregnated beech veneers shows a significant improvement in the dimensional stability after air plasma pretreatment of the veneers due to a significantly higher degree of loading. In contrast, no improvement in the dimensional stability of plywood samples from native beech veneers was achieved (Wascher 2017b). This observation confirms the results of the shear strength tests. Plywood panels made of plasma-treated, thermally-modified and unmodified, and melamine-impregnated (25% and 50% concentration) beech veneers show little delamination along with an increased shear strength compared to plywood panels made of untreated veneers after shrinkage/swelling stress (Wascher 2017a). Furthermore, no significant differences in the mechanical properties (compressive strength and bending strength) of plywood were found among all the variants tested, with the exception of an improvement in the tensile strength of plywood made from thermally-modified beech veneers.

CONCLUSIONS

The review of published results demonstrates the effectiveness and suitability of oxygen-containing plasmas as a prior process step for subsequent impregnation of wood veneers with waterborne modification agents and/or as a prior process step for plywood production. The investigations showed significantly improved wetting behaviour in addition to improved uptake of water and waterborne modification agents for most types of veneers when air-plasma-treated. Plywood made of plasma pre-treated and subsequently modified veneers showed an enhanced dimensional stability compared to plywood made of untreated and modified veneers, while the mechanical properties remained on the level of conventionally produced plywood or showed slightly improved properties.

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Saturated gaseous ammonia treatment for improved densification of beech wood – Sorption, mechanical and dynamic properties

Mario Zauer, Tobias Dietrich, Herwig Hackenberg and André Wagenführ

Technische Universität Dresden, Institute of Natural Material Technology, 01062 Dresden, Germany [email: mario.zauer@tu-dresden.de]

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ABSTRACT

The present paper deals with saturated gaseous ammonia treatment and subsequently densification of European beech (*Fagus sylvatica* L.) aimed at improved mechanical, dynamic and colour properties to substitute tropical wood species. On focus was the use of the modified material for fingerboards in electric guitars to substitute Indian rosewood (*Dalbergia latifolia* Roxb.) most used in this area. The need resulted from the currently highly regulated tradeability of all *Dalbergia*-species since January 2017.

On the one hand, beech was treated with gaseous ammonia only. On the other hand, beech was treated with gaseous ammonia and following densified in radial direction with a degree of densification of 20%. In each case the ammonia treatment was conducted at isothermal conditions at 20°C for 0.5 h and 6 h.

The investigations involved physical (density, sorption and swelling behaviour), mechanical (hardness, bending strength and modulus of elasticity) and dynamic (damping, dynamic shear modulus and dynamic modulus of elasticity) tests. In addition to untreated and treated beech untreated Indian rosewood were tested to compare the corresponding properties.

The results show that with increasing ammonia treatment time the density of beech increase from 730 kg m^{-3} (untreated) up to 920 kg m^{-3} owing to the well-known “collapse” of the wood structure after the treatment procedure. Additional densification leads to further increase of the density up to 1130 kg m^{-3}. Therefore, for the most part, all mechanical properties improve owing to the treatments used. However, the low damping values and relative high dimensional stability at moisture changes of rosewood could not be reached. Remarkable is the reduction of the swelling anisotropy, with respect to the tangential and radial direction of the wood, up to 1.3 owing to the ammonia treatment procedure for 6 h used in this study.

INTRODUCTION

It is well known that transverse compression of wood leads to a denser, stiffer and harder material (Seborg and Stamm 1941). However, densified wood tends to spring back in its original shape, which is well-known as the so-called “spring back effect”. Hence, the wood loses the improved properties previously achieved. Thus, a proper fixation of the shape is necessary. On the one hand, ammonia treatment of wood leads to an improved plasticisation compared to hot steam. On the other hand, ammonia treatment of wood changes the crystalline parts of the cellulose, which are responsible for spring back of the densified wood structure due to moisture stress (Parham 1971). That is, ammonia plasticized wood can be formed into complex shapes and, in contrast to water plasticisation, the achieved shape is stable after removing the ammonia even after contact with liquid water. Furthermore, the wood stained to brown or dark brown owing to ammonia treatment in dependence of the treatment intensity (time, temperature, pressure). Thus, the mentioned properties of ammonia treated wood make it suitable to substitute tropical wood species for many applications, such as musical instruments.

Fingerboards used for plucking instruments, such as electric guitars, are mostly made out of Indian rosewood (*Dalbergia latifolia* ROXB.). Beside its excellent mechanical properties, high dimensional stability, hardness and wear resistance, the colour and texture are main factors to uses this wood species. Indian rosewood and other *Dalbergia* species are listed as endangered in the IUCN (International Union for Conservation of Nature) red list owing to overexploitation. Consequently, at the 17th CITES Conference (convention on international trade in endangered species) all *Dalbergia* species which were not listed in CITES appendix 1, were listed on CITES appendix 2 since 01.01.2017. Hence, trading *Dalbergia* species is strongly limited under special conditions and under strict control mechanism. Besides using other tropical hardwoods as tone woods which are not listed in CITES, the most sustainable solution is using domestic wood species from sustainable forest management. Compared to the commonly used tropical hardwood species, European species are not reaching the dark colour and the required mechanical and acoustic properties without a thermal modification (Sproßmann 2017) or a chemo-mechanical modification (Dietrich 2014).

The above-mentioned ammonia treatment in combination with densification of wood has been known for several decades. However, there are no industrial productions of materials modified in this way (Paril et al. 2014). Therefore, the aim of this study was to modify beech by means of gaseous ammonia treatment and subsequently densification to improve the appropriate properties similar to Indian rosewood to substitute the latter in fingerboards of electric guitars.

EXPERIMENTAL

Material

Heartwood of untreated and treated European beech (*Fagus sylvatica* L.) as well as untreated Indian rosewood (*Dalbergia latifolia* Roxb.) as reference material was investigated. On the one hand, solely ammonia treated samples (AT) were produced. On the other hand, ammonia treated and subsequently densified samples (ATD) were produced.

Specimens for modification were sawn, planed and grinded to final dimensions of 9.8 x 31 x 200 mm³ (R x T x L). Before treatment, all samples were conditioned at 20°C and 65% relative humidity (RH) until they achieved a constant mass. Ammonia treatment (AT) was conducted at a lab-scale using gaseous anhydrous ammonia (purity grade 99.98%) in an autoclave by means at constant vapour pressure at 0.9 under isothermal conditions at 20°C for both 0.5 h and 6.0 h.

Densification of ATD beech was conducted in radial main cutting direction of the wood with a degree of densification of 20% based on the original dimension. The densification procedure took place at 20°C and the velocity for densification was 1 mm min^{-1}.

After treatment procedures all samples were vented and gently oven dried to remove the ammonia. In this case, the densified samples were kept in the form-fixed state by means of fixed aluminium plates to prevent a possible spring back of the densified wood structure. Drying was conducted by means of different temperature steps with a final temperature of 103°C.

Following all specimens were conditioned at 20°C and 65% relative humidity (RH), until they achieved a constant mass, as well as sawn, planed and grinded to final dimensions of 6.5 x 28 x 190 mm³ (R x T x L). In the latter case, finishing was carried out symmetrically from each of both outer surfaces. Each series comprised 12 specimens.

Methods

The investigations included the determination of raw density (DIN 52182) and equilibrium moisture content (EMC) (DIN EN 13183-1).

Experimental modal analysis (EMA) with free-free boundary conditions was used to determine dynamic modulus of elasticity (dynamic MOE), dynamic shear modulus at longitudinal-tangential plane (dynamic GLT) and damping (loss coefficient). The EMA used, is a method to investigate the dynamic properties (mode shape, Eigenfrequencies and damping) of structures. A detailed description of this technique is given by Möser (2000) and Natke (1983). In our study the impulse excitation was provided using an impact hammer. The complex vibrations were measured by an accelerometer located diagonally to the excitation site at the other end of the sample. The specimen was supported horizontally by two thin threads located at the nodes of vibration of the first bending mode (free-free boundary conditions). The frequency range was between 0 kHz and 5 kHz. A detailed description and calculation of the conducted tests are given by Sproßmann *et al.* (2017).

The modulus of elasticity (MOE) and modulus of rupture (MOR) were determined by means of a three-point bending test in accordance to DIN EN 310 with a span of the samples of 150 mm. Furthermore, Brinell hardness (HB) was measured perpendicularly to the grain in radial direction in accordance to DIN EN 1534.

The swelling behaviour was investigated by means of three water storage cycles each with following drying process at 103°C. The maximum swelling of both radial (α_r) and tangential (α_t) direction was calculated after the third water storage cycle according to DIN 52184. In this context, anti-swelling efficiency (ASE) was determined (Eqn. 1):

$$\text{ASE } (\%) = [(\alpha_{UV} - \alpha_{TV}) / \alpha_{UV}] \text{ x } 100 \qquad (1)$$

where α_{UV} is the maximum volumetric swelling of untreated beech and α_{TV} is the maximum volumetric swelling of the treated wood (AT, ATD).

Except for tests of dimensional stability, all investigations were conducted at 20°C and 65% RH.

RESULTS AND DISCUSSION

The results (Table 1) show that the density of beech increases with the treatment intensity (AT, ATD), as expected. Ammonia treatment for 6 h (AT 6.0) leads to higher density by almost a third compared to untreated beech. This can be explained owing to the closure of the cell lumina and owing to the partial reduction of pore volume of the cell walls after removal of the ammonia from the wood (Bariska 1975), also known as “collapse” after ammonia treatment of the wood (Parham 1971, Pollisco et al. 1971). Furthermore, EMC decreases with increasing AT time by almost a third for AT 6.0 beech compared to untreated beech. In contrast, Weigl et al. (2009) reported about an increase of EMC of gas phase ammonia treated beech and other hardwoods, respectively. They explained the increased EMC with an increased polarity of the treated wood. Parham (1971) reported an increase in crystallinity of previously amorphous areas of cellulose, leads in a decrease of EMC (Bariska 1975), which is in line with our results.

Additional densification of AT beech (ATD) leads to further increase of the density up to appr. 55% and a significantly decrease of the EMC by appr. 33% for ATD 6.0 beech compared to untreated beech (Table 1). In this case, the density is much higher and EMC is even much lower than for rosewood.

Table 1: Comparison of the determined raw density, equilibrium moisture content (EMC), maximum swelling in radial (α_r) and tangential (α_t) direction and anti-swelling efficiency of the untreated and treated beech and untreated rosewood, respectively

Sample		**Raw density[a] [kg m^{-3}]**	**EMC[a] [%]**	**α_r [%]**	**α_t [%]**	**ASE [%]**
Beech	Untreated	730	8.8	6.8	13.2	-
	AT 0.5	730	7.5	8.4	16.6	-25
	ATD 0.5	860	7.6	15.4	14.6	-15
	AT 6.0	920	6.6	16.8	22.2	-95
	ATD 6.0	1130	5.9	26.3	20.5	-135
Rosewood	Untreated	780	7.7	2.9	6.4	-

[a]determined at conditioned state at 20°C and 65% RH

However, although the EMC of both AT and ATD beech is reduced the swelling behaviour is strongly increased, which reflects the increased maximum swelling value of the treated wood (Table 1). Thus, ASE is even negative. One main reason is probably the substantially increased density and thus the much higher proportion of cell-wall material of both AT and ATD beech compared to untreated beech. Remarkable is the decreased swelling anisotropy, ratio of the tangential to radial direction of the wood, of AT 6.0 beech (appr. 1.3) compared to untreated beech (appr. 2). In case of ATD beech, the radial swelling is significantly higher than in tangential direction owing to the substantially higher proportion of cell-wall material caused by the densification in radial direction. In this connection, the swelling anisotropy, ratio of the radial to tangential direction, is appr. 1.3. Unfortunately, the very high dimensional stability of rosewood was not reached. Hence, untreated beech and treated beech used are regarding the dimensional stability clearly at a disadvantage compared to rosewood. An additional subsequently thermal modification process after both AT and ATD is capable to increase the dimensional stability of the treated wood (Paril 2014).

Referring to the results of static and dynamic tests (Figure 1): Brinell hardness, dynamic GLT, MOR and both static MOE and dynamic MOE substantially increases owing ATD 6.0 of beech. This is obviously a consequence of the increased density and decreased EMC of ATD 6.0 beech compared to untreated beech. Especially, the high hardness reflects a high wear resistance, which is essential for fingerboards in electric guitars due to the high scratch stress during the guitar playing in dependence of the playing technique of the individual musician (e.g. bending of the strings). Furthermore, a high shear modulus counteracts torsion of the guitar neck caused by the different string tensions. A low shear modulus tends to results in a torsional twisting of the neck while playing. Thus, string buzzing and other disturbing noises while playing can occur. Therefore, woods for fingerboards need to have a high shear modulus (Sproßmann 2017). Damping of wood is very important for wood used for guitar making. It withdraws the energy owing to internal friction which otherwise is available for sound radiation. Unfortunately, the determined damping values of both untreated and treated beech are much higher than these of rosewood (Figure 1b). Both AT and ATD of beech even increase the damping compared to untreated beech. The increased density cannot be the cause, taking into account of both AT 6.0 and ATD 6.0 beech. The cause is perhaps the extremely high swelling behaviour, associated with the formation of cell wall internal small cavities, which leads to high internal friction, thus high damping. The formations of small cavities in ATD beech is probably lower than these in AT beech owing to the mechanical densified wood structure.

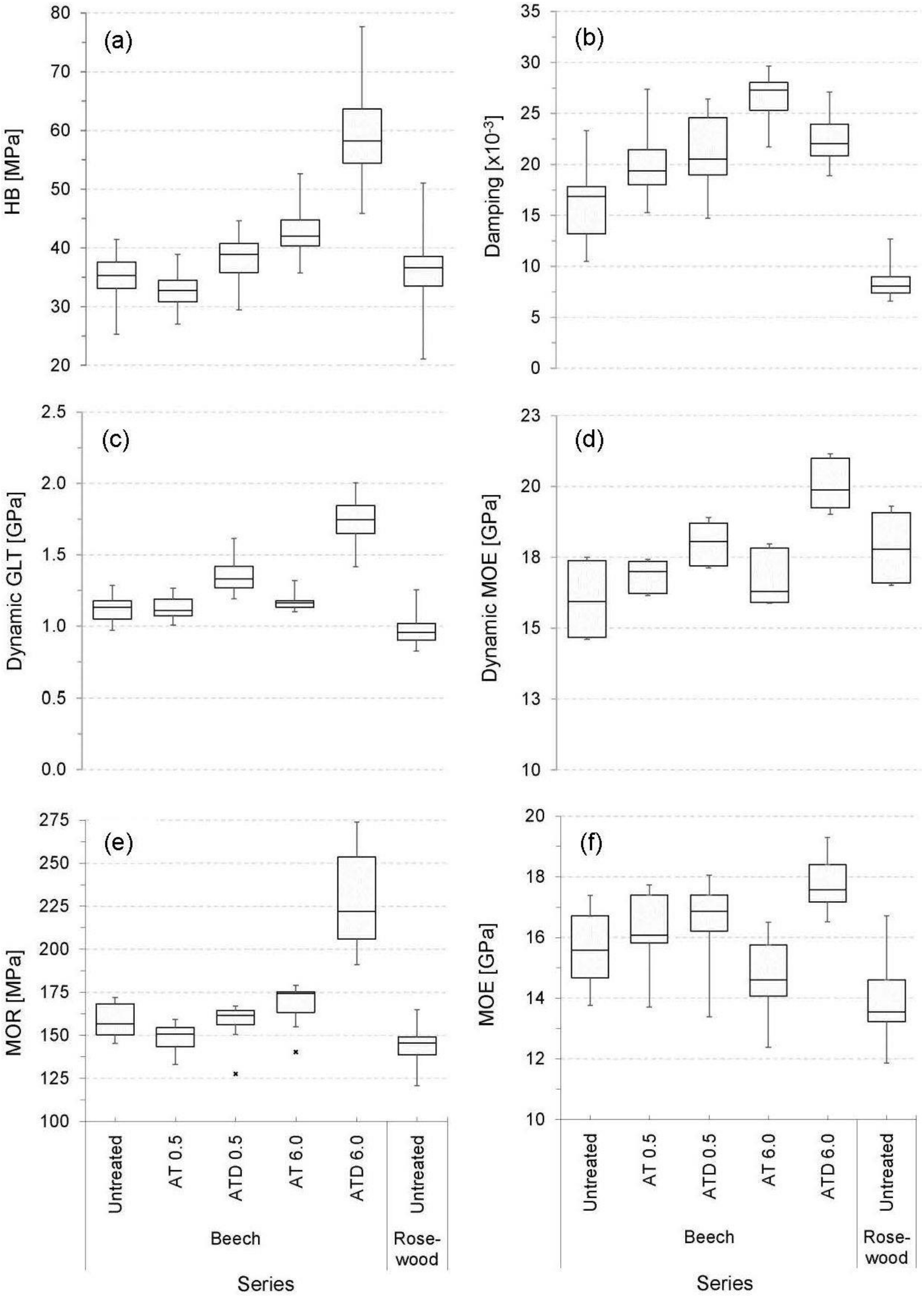

Figure 1: Comparison of Brinell hardness (a), damping (b), dynamic shear modulus at LT plane (c), dynamic modulus of elasticity (d), modulus of rupture (e) and static modulus of elasticity (f) of untreated and different treated beech plus untreated rosewood

CONCLUSIONS

Both solely gaseous ammonia treatment and in combination with a densification procedure leads to increased density, decreased equilibrium moisture content and mostly to improved mechanical properties of European beech. However, both swelling behaviour and damping values of beech increase owing to the treatments used, which reflects a disadvantage compared to rosewood most used as fingerboard material in electric guitars. Nevertheless, there is a chance that the treated wood can substitute rosewood in this area, also due to the staining toward a dark brown colour.

ACKNOWLEDGEMENTS

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Water vapour diffusion through acetylated wood with different weight percent gain (WPG)

Ava Khodabakhshi Koulaei [1], Asghar Tarmian[2], Davood Efhamisisi[3],
Ali Abdulkhani[4]

[1]Department of Wood and Paper Sciecne & Technology, University of Tehran, Iran [email: ava.khodabakhshi@ut.ac.ir]
[2]Department of Wood and Paper Sciecne & Technology, University of Tehran, Iran [email: tarmian@ut.ac.ir]
[3]Department of Wood and Paper Sciecne & Technology, University of Tehran, Iran [email:efhami@ut.ac.ir]
[4]Department of Wood and Paper Sciecne & Technology, University of Tehran, Iran [email: abdulkhani@ut.ac.ir]

Keywords: Acetylated wood, Water vapour diffusion, Weight percent gain (WPG)

ABSTRACT

Changes in water vapour diffusion of Norway spruce and poplar wood after modification by acetylation process with different weight percent gain (WPG) were evaluated. The oven-dried cylindrical wood specimens with 5mm in thickness and 48 mm in diameter were acetylated using liquid acetic anhydride at reaction temperature of 120 ºC for 1, 2, 4 and 24 h. The diffusion coefficients were then measured perpendicular to the grain using cup method under steady-state conditions. The obtained WPG ranged from 10.1 to 21.1 for Norway spruce and from 8.1 to 17.6 for poplar, depending on the reaction time. Acetylation had no significant effect on the water vapour diffusivity of Norway spruce, whereas the diffusivity of poplar reduced due to acetylation. Our results confirm that the effect of acetylation on the water vapour diffusion rate in wood is species dependent.

INTRODUCTION

Acetylation is one of commercial chemical modification technologies of wood. It is the reaction of accessible hydroxyl (-OH) groups in the cell wall polymers with acetic anhydride. By changing the hydrophilic hydroxyl groups in the cell walls into the hydrophobic acetyl groups, a number of wood properties, such as moisture sorption, wettability, dimensional stability and decay resistance are improved (Ramsden *et al.* 1997, Rowell *et al.* 2014, Huang *et al.* 2018). Water vapor diffusion refers to the movement of the vapor molecules through a diffusible material like wood. The main driving force for diffusion is the concentration gradient based on Fick's law. The rate of water vapor diffusion in wood as a building material is important in several applications (e.g. drying, coating, the life of outdoor wooden structures, packaging). The diffusion coefficient of wood depends on the numerous parameters, such as density, moisture content, annual ring orientation and porous structure (Siau 1984, Perré 2007). It is well known that more cell-wall substance traversed per unit distance offers more resistance to the diffusion. However, Tarmian *et al.* (2012) found that the diffusion is not only controlled by wood density. They found that the mass diffusivity of beech is higher in tension wood than in normal wood in spite of almost similar density values, probably due to the ease of diffusion in the gelatinous layer. The water vapor diffusion rate in wood was found to be changed after steaming and microwave radiation (Dashti *et al.* 2013, Sayar and Tarmian 2013). Rousset *et al.* (2004) also reported that the mass diffusivity of poplar reduces after thermal modification at 200 ℃, probably due to the chemical modification of the cell wall. The main purpose of the present study is to find the role of accessible OH groups of wood in the water vapor diffusion rate by substituting them with acetyl groups at different degree of acetylation.

EXPERIMENTAL

Wood sampling

Cylindrical specimens with 48 mm in diameter and 5 mm in length were cut from the sapwood of Norway spruce and poplar. The wood specimens were first extracted with a mixed solution of ethanol and acetone (v/v, 1:2) for 8h. Then, they were dried at 103 ± 2℃ for 24h and the oven-dried weights of the specimens were measured.

Acetylation process

Acetic anhydride [$(CH_3CO)_2O$] used in this study was purchased from Pars Co. in Iran. A vacuum/pressure method was employed to impregnate the oven-dried wood specimens with the anhydride. After initial vacuum (60 kPa, 30 min), they were saturated by the solution at the pressure of 400 kPa for 2h. After impregnation, the specimens were exposed to the atmospheric pressure overnight at room temperature. The impregnated specimens were then wrapped with aluminum foil and heated at 120℃ for different reaction times (1, 2, 4, and 24h). After acetylation, the samples were washed with acetone and distilled water for 48h. They were finally oven dried at 103 ± 2℃ for 24h and weighted to determine the weight percent gains (WPG).

Measurement of water vapor diffusion

Water vapor diffusion of control and modified specimens was measured by cup method based on first Fick's law under steady state conditions. The lateral surfaces of the cylindrical specimens were first coated by epoxy resin to avoid the vapor leakage. They were then used as lids over the cups. The saturated salt solution of sodium chloride was used to provide a relative humidity (RH) of about 75% inside the cups. The cups (vapormeters) were placed inside a climatic room (60% RH, 20℃) to create a vapor pressure gradient. The reader can refer to Tarmian et al. (2012) for further details of the experimental set up. The weight of cups was recorded every 48 h until a constant weight change (mass flow) was reached. The dimensionless diffusivity (f) was calculated by the following equation:

$$f = \frac{Q}{D_v A} \frac{L}{(RH_2 - RH_1) P_{vs}(T)} \frac{RT}{M_v} \tag{1}$$

where Q is the water vapor flux ($kg.s^{-1}$), A is the cross section of sample (m^2), M_v is the molar weight of vapor ($kg.mole^{-1}$), RH_1 is the relative humidity inside the climatic room, RH_2 is the relative humidity inside the cup, R is the constant of perfect gas, L is the sample thickness (m), P_{vs} is the pressure of saturated water vapor (kPa) at the temperature of $T(K)$ and D_v is the water vapor diffusion coefficient in air, and $D_v=24.2\times10^{-6}\ m^2s^{-1}$. The measurement was carried out with five repetitions for each treatment.

RESULTS AND DISCUSSION

The average WPG ranged from 8.1 to 17.6 for poplar and from 10.1 to 21.1 for Norway spruce, depending on the reaction time (Figure 1). Increasing the reaction time was found to have a greater effect on the WPG of Norway spruce than poplar. The WPG determines the degree of acetylation and at higher level of WPG, more accessible hydroxyl groups of wood can be acetylated. Popescu et al. (2014) reported that reduction in the accessible OH content due to acetylation was well correlated with the weight gain due to acetylation. Poplar showed more water vapor diffusivity than Norway spruce. Acetylation had no significant effect on the water vapor diffusivity of Norway spruce, whereas the acetylated poplar showed more resistance to the vapor diffusion when compared to the unmodified wood (Figure 2). The water vapor diffusion in poplar wood reduced by 32.9 % after acetylation at a WPG of 15.5. Other wood-water relation variables of wood, such as wettability, equilibrium moisture content (EMC) and fiber saturation point (FSP) are reduced as a result of acetylation (Papadopoulos and Hill 2003, Popescu *et al.* 2014, Passarini *et al.* 2017). The chemical bond forming between the wood and acetic anhydride reduces the hydroxyl groups of wood, which consequently prevents the interaction of water with wood. In contrast to poplar, we found no significant correlation between the WPG and diffusion coefficient of Norway spruce at confidence level of 95% (Table 1), which indicates that the water vapor diffusion of wood is not only controlled by the hydroxyl groups.

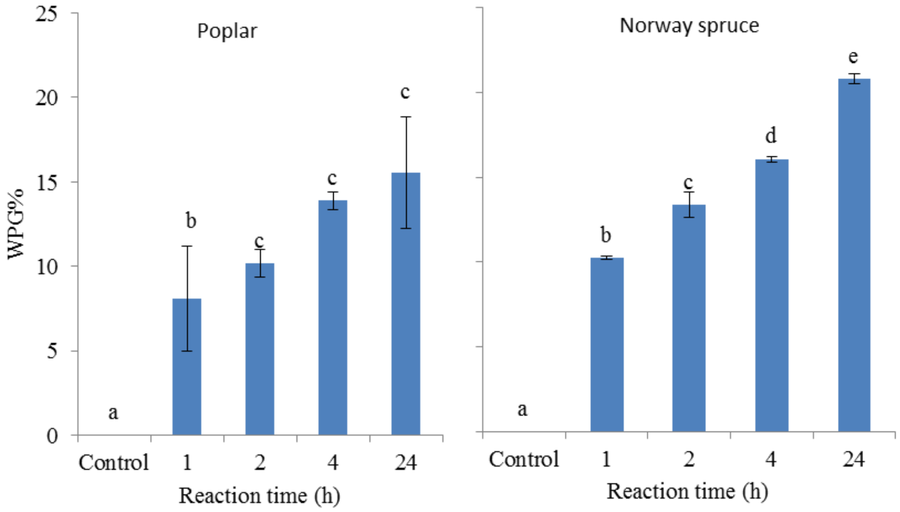

Figure 1: Weight percent gain (WPG) of poplar and Norway spruce after acetylation at different reaction times

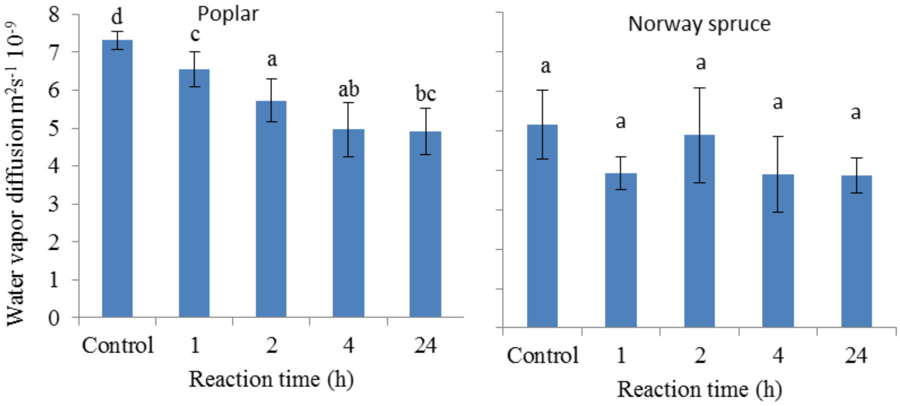

Figure 2: Water vapor diffusion in control and acetylated poplar and Norway spruce

Table 1: Pearson correlation between the WPG and diffusion coefficient

Species	Sig.	Pearson correlation
Poplar	0.000**	-0.796
Norway spruce	0.041	-0.346

***Correlation is significant at the 0.01 level*

CONCLUSIONS

The purpose of this study was to examine water vapor diffusion through acetylated wood with different weight percent gain (WPG). The following conclusions can be drawn:

- The effect of acetylation on the water vapor diffusion coefficient of wood is species dependent. Acetylation had no significant effect on the vapor diffusivity of Norway spruce, while the diffusion rate in poplar reduced due to acetylation.
- Although no significant correlation was observed between the water vapor diffusion of Norway spruce and the degree of acetylation, the correlation was significant for poplar at the 0.01 level.

Overall, our results confirm that the water vapor diffusion through wood is not solely controlled by the accessible OH content. Changes in the water vapor diffusion after acetylation may be due to alteration in the porous structure of wood. Therefore, study on the porosity of acetylated wood seems to be essential to in-depth understand the effect of acetylation on this property.

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SESSION FOUR A

Properties 1

The potential for the use of acetylated wood in musical instruments making

Stergios Adamopoulos[1], Sheikh Ali Ahmed[1], Chiel Lankveld[2]

[1]Department of Forestry and Wood Technology, Faculty of Technology, Linnaeus University, 351 95 Växjö, Sweden [email: stergios.adamopoulos@lnu.se; sheikh.ahmed@lnu.se)]
[2]Accsys Group, Westvoortsedijk 73, 6827 AV Arnhem, The Netherlands [email: Chiel.Lankveld@accsysplc.com)]

Keywords: Acoustic conversion efficiency, damping, equilibrium moisture content, free-free flexural vibration, volumetric shrinkage

ABSTRACT

In musical instrument making, less expensive wood species and materials with good characteristics and acoustical properties can provide potentials to find alternatives to the traditional exotic wood species used today. Modified wood could be such a choice if shows similar sound characteristics to wood coming from endangered and expensive tropical species with problematic commercial availability. In musical instruments, the overall functionality depends on the contribution of wood to different material performance indexes like sound radiation coefficient (*R*), characteristic impedance (*z*) and acoustic conversion efficiency (*ACE*). In this study, the performance indexes were measured for acetylated beech, maple and radiata pine and compared with these obtained for the reference wood materials maple, mahogany, alder and ash. A non-destructive free-free flexural vibration test method was used at constant temperature (20^{o}C) but in different humid conditions- dry (35% RH), standard (65% RH) and wet (85% RH). Dimensional changes in the different humid conditions were also taken in account. Acetylated wood showed lower *EMC* with higher dimensional stability at each humidity level as compared with the reference wood materials. These properties are considered important factors for making quality musical instruments. Based on the acoustical properties, acetylated wood materials, especially radiata pine, showed good potential for use for musical instruments where specific characteristics of sound are required. However, the other types of acetylated wood can also be used for specific musical instruments.

INTRODUCTION

The quality of a musical instrument depends on the type of wood material used in different parts and the harmony among them when it is constructed. Tropical hardwoods are typically used in musical instruments making (Bucur 2006). Nowadays, the demand to replace tropical wood in musical instruments is higher due to problems related with the sustainability of tropical forests and their commercial availability at high prices (Torres *et al*. 2015). However, choosing alternative wood species for musical instruments should take into account several parameters related to anatomical features, physical, mechanical, acoustical and chemical properties. Alternative wood species that are less expensive and more available are thus not taken in consideration, as they possess inferior acoustical properties. Furthermore, unmodified wood can also change its acoustic behavior over time and in different moisture conditions. On the other hand, high quality wood for musical instruments making is getting harder to find as well as more expensive too (Torres and Torres-Martínez 2015). If modified wood shows similar sound characteristics to naturally aged wood, it could also be suited for restoration and reconstruction of old musical instruments. Thus, there is a huge potential of using such alternative wood materials in musical instrument industry in case that wood modification can ensure the improvement or stabilization of the acoustical properties of wood. A wise selection of the wooden raw materials for musical instruments making including the modified ones is thus feasible. In such a case, modified wood could be a good candidate for instrument making due to its favourable attributes such as increased dimensional stability, reduced water uptake, improved hardness, and resistance to weathering. Usually, static and dynamic mechanical properties remain unchanged or even increase depending on the modification method and intensity (Militz *et al*. 1997, Rowell 2006). Among different types of wood modification, acetylation is the most successful chemical modification method and the commercial product (Accoya®) is offered by Accsys Technologies PLC, UK. Reaction between the chemical molecule of acetic anhydride and the -OH groups of the wood substrate takes place to generate acetylated wood. In this process, one acetyl group is attached to one -OH group without polymerization and results in significant reduction of moisture absorption (Rowell *et al*. 2009).

Acetylated wood has increased durability due to alterations in material properties. In addition, the technology results in improved wood properties like better dimensional stability, reduced water uptake, and improved hardness. The enhanced properties of modified wood with pleasant appearance not only ideal for interior or exterior uses but also acoustical properties are modified for their applicability in musical instrument makings (Rowell *et al*. 2008, Rowell 2013). However, there is still lack of information on the acoustic performance of acetylated wood at different humidity conditions. It is also well known that wood is a hygroscopic material and it changes its dimensions as the ambient humidity changes, which eventually changes the dimensions of wood products too. This could affect the tone quality of wooden musical instruments.

This present work determines the acoustical properties of acetylated wood at different humid conditions for its potential use in musical instruments making. It is also worthwhile to know how the use of acetylated wood could contribute to satisfy the increasing demand of high-quality wood for musical instruments. A first step is thus to evaluate the acoustical properties of different acetylated wood materials as it is anticipated that their acoustic behaviour will vary little under different climatic conditions.

EXPERIMENTAL

Materials selection and preparation

Commercially produced acetylated beech (*Fagus sylvatica* L.), maple (*Acer* spp.) and radiata pine (*Pinus radiata* D. Don) from Accoya®, Accsys Technologies PLC, Arnhem, The Netherlands were collected for this study. In addition, light weight swamp ash (*Fraxinus* spp.), maple (*Acer saccharum* Marshall), alder (*Alnus glutinosa* (L.) Gaertn.) and mahogany (*Swietenia macrophylla* King) wood pieces were used as reference material as they are commonly used in musical instruments. Test samples were sawn and planed to a final dimension of 350 (longitudinal) × 25 (tangential) × 12.5 (radial) mm. Three samples were prepared for every type of material giving a total of 21 samples. Additional samples from every category were also machined for measuring the moisture content and dimensional changes. Samples were acclimatized in three humid conditions of dry- 35%, standard- 65% and wet- 85% RH at a constant temperature of 20ºC.

Physical properties

Densities of samples were measured by taking their weight and volume at the respective humid conditions (35%, 65% and 85% RH at a constant temperature of 20ºC). On additional samples, MC determinations were made after oven-drying at 103±2ºC for 24 h. Radial and tangential shrinkage was measured on 5 samples with dimensions of 25 × 25 × 0.5 mm^3 (radial × tangential × longitudinal) and longitudinal shrinkage on 10 × 10 × 100 mm^3 (radial × tangential × longitudinal) samples. Samples were covered with cellulose sponge cloths saturated with water for 2 weeks. Then the radial, tangential and longitudinal dimensions were measured using a calliper at the closest 0.02 mm on the samples after complete saturation and oven-drying at 103±2°C. Volumetric shrinkages were calculated based on the radial, tangential and longitudinal shrinkages.

Acoustical properties

Measured acoustical properties of wood materials were the speed of sound (c) within the material, specific acoustic impedance (z), sound radiation coefficient (R), and acoustic conversion efficiency (ACE). To determine these properties, dynamic moduli of elasticity (MOE_{dyn}) need to be measured. Thus, dynamic tests were performed (three repetitions) based on free-free vibration techniques (Figure 1). In this resonance method, the BING system (Beam Identification by Non-destructive Grading by CIRAD, Montpellier, France) was used, which is designed to evaluate the mechanical properties of rigid materials using vibration analysis (Brancheriau *et al*. 2007). Flexural vibration was used to determine the MOE_{dyn} and the internal friction of the wood material by employing the BING® version 9.6.2 (build 88) software. The signal sampling frequency was 40000 Hz with spectral acquisition of 16384 points.

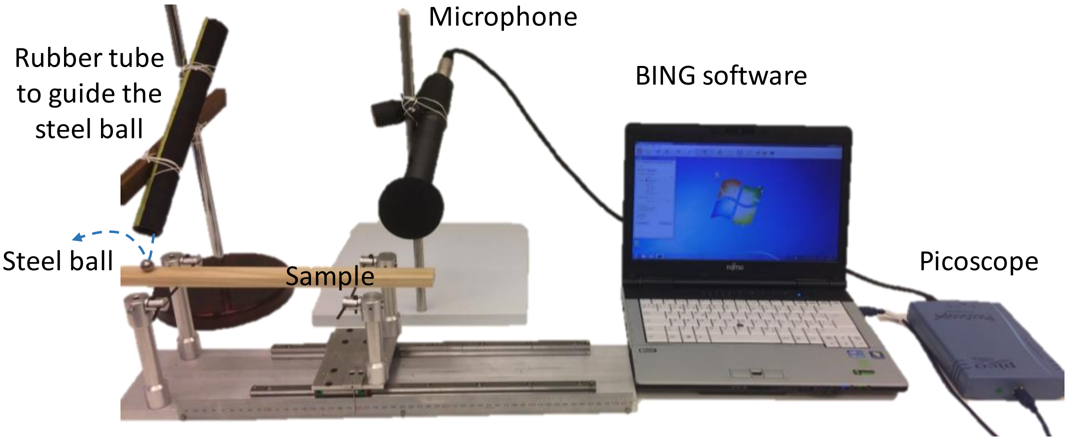

Figure 1: Stage setup for BING test

The acoustical properties were determined by the following equations:

$$c = \sqrt{\frac{MOE_{dyn}}{\rho}} \qquad (1)$$

where, c is the sound speed (m s^{-1}), MOE_{dyn} is the dynamic modulus of elasticity (Pa) and ρ is the density (kg m^{-3}).

$$z = c\rho = \sqrt{MOE_{dyn} \times \rho} \qquad (2)$$

where, z is the specific acoustic impedance or characteristic acoustic impedance (MPa s m^{-1}).

$$R = \frac{c}{\rho} = \sqrt{\frac{MOE_{dyn}}{\rho^3}} \qquad (3)$$

where, R is the sound radiation coefficient (m^4 kg^{-1} s^{-1}) and $tan\delta$ is the damping coefficient.

$$ACE = \frac{\sqrt{\frac{MOE_{dyn}}{\rho^3}}}{\tan\delta} \quad (4)$$

where, *ACE* is the acoustic conversion efficiency ($m^4\ kg^{-1}\ s^{-1}$).

$$\tan\delta = \frac{\alpha_1}{\pi f_1} \quad (5)$$

where, α_1 is the temporal damping associated with f_1.

Data analysis

The *ACE* data were analysed using the statistical software package IBM SPSS Statistics, Version 23 (IBM Corporation, New York, USA). One-way analysis of variance (ANOVA) was applied to determine whether *ACE* were significantly different among different wood samples. A 5% level of significance was used to detect differences. When significant differences were found, Duncan's multiple-range test was performed.

RESULTS AND DISCUSSION

The present study examined whether acetylated wood has the necessary acoustic qualities under different humid conditions (dry, standard and wet) to contribute to the supply of raw materials for wooden musical instruments. The wood materials examined were acetylated beech, maple and radiata pine. Various acoustical and physical properties were compared with these obtained from maple, mahogany, ash and alder, which are generally used in musical instruments making. Physical properties included equilibrium moisture content *EMC* and volumetric shrinkage. The acetylated wood showed low *EMC* values at each humidity level (35%, 65% and 85%) and high dimensional stability, which are considered important factors for making quality musical instruments (Table 1).

Acetylated wood shows low EMC at various relative humidity levels due to the replacement of some hydroxyl groups of the cell wall polymers with bonded acetyl groups, and as a result, the hygroscopicity of wood is reduced. In detail, hydroxyl sites are esterified with acetyl groups and thus the cell wall has fewer sites to which water can be sorbed (Hill 2006). The lower cell wall moisture content provides wood with improved dimensional stability, and such wood stability is quite an important factor needed for quality musical instruments making. Among the three types of acetylated wood, acetylated radiata pine showed lower *EMC* at each of three humidity levels and higher dimensional stability (2.11% in terms of volumetric shrinkage).

Table 1: Equilibrium moisture content (EMC) at different relative humidity (RH) levels and total volumetric shrinkage of acetylated and reference wood materials

Type of wood	***EMC* at 20ºC**			**Volumetric shrinkage (%) from saturation to oven dry**	
	35% RH	**65% RH**	**85% RH**	**Mean**	**SD**
Act beech	4.0	4.5	6.0	3.80	0.14
Act maple	3.9	5.5	7.0	3.64	0.18
Act RP	2.5	3.4	4.7	2.11	0.13
Maple	7.3	10.5	17.5	15.85	0.03
Mahogany	9.1	11.1	17.4	5.54	0.32
Ash	7.4	10.5	17.8	11.80	0.23
Alder	7.0	10.0	13.4	14.29	0.02

Act: acetylated, RP: radiata pine, SD: standard deviation

Flexural vibration with a free-free end condition was used to determine the MOE_{dyn} and $tan\delta$ of wood samples. Using MOE_{dyn} and ρ values, the MOE_{dyn}/ρ was calculated as it is an important parameter, which has a direct relation with c, R and ACE (see Equations 1, 3, 4). In general, wood with high value of MOE_{dyn}/ρ combined with a low $tan\delta$ is accepted for soundboards of pianos, guitars and violins (Matsunaga *et al*. 1996). The MOE_{dyn}/ρ value was found higher for acetylated wood samples than the reference ash and alder (Figure 1). However, the highest MOE_{dyn}/ρ was found in mahogany. With the decrease in moisture content, MOE_{dyn}/ρ values were increased whilst it was just the opposite for the property, $tan\delta$. This trend is in accordance with the findings of Akitsu *et al*. (1993).

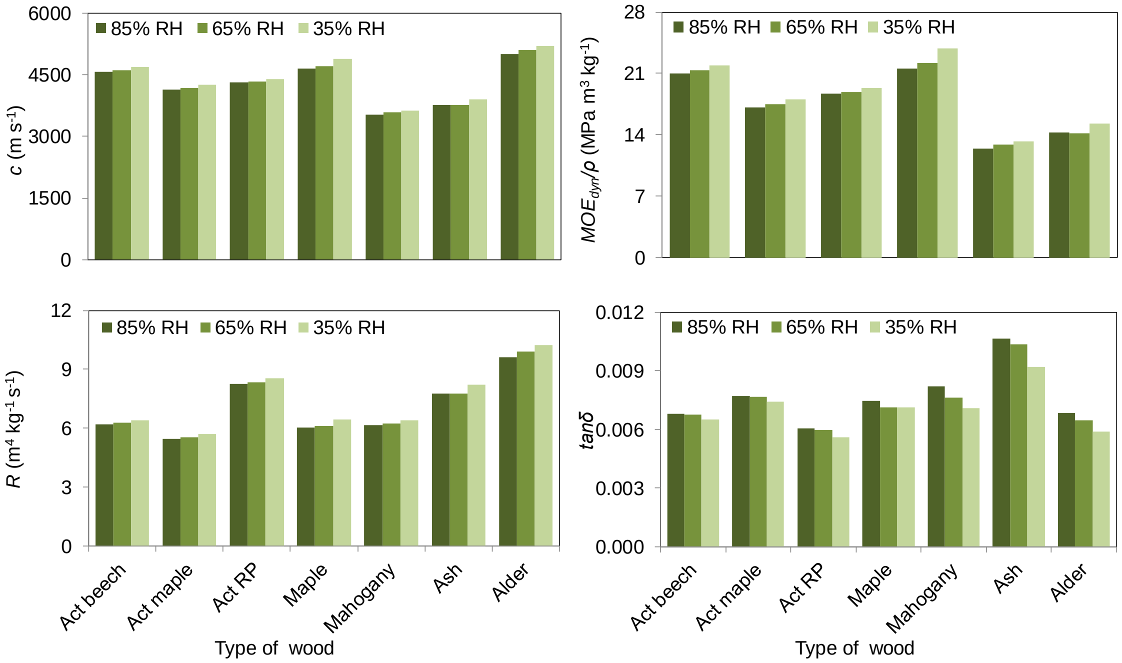

Figure 2: Speed of sound (c), specific dynamic modulus of elasticity (MOE_{dyn}/ρ), sound radiation coefficient (R) and damping coefficient (tanδ) in acetylated and reference wood materials at different relative humidities. Act: acetylated, RP: radiata pine

Density and MOE_{dyn} are related to the speed of sound, which is decreased with an increase in moisture content. The speed of sound in wood is proportionally influenced by *MOE* and density (see Equation 1). Acetylated wood with high sound velocity and low internal damping best facilitated the transmission of vibrational energy. In this experiment, it was also observed that speed of sound was higher in samples with lower moisture content (Figure 2). However, along with this factor, other acoustical properties play also a role to determine the quality wood for musical instruments.

The sound radiation coefficient or acoustic constant, R, is a measure of the vibration within the wood as it is damped by radiating sound. A large R of the wood material is needed to produce a loud sound. In other words, a higher R increases the resonance quality. In this study, it was found that acetylated wood had R-values ranging from 5.45 to 8.53 m^4 kg^{-1} s^{-1} (Figure 2). R values > 8 m^4 kg^{-1} s^{-1} are ideal for soundboard making. However, wood for instruments like xylophone bars, violin bows, and wind instruments have R-values between 4 to 8 m^4 kg^{-1} s^{-1} (Wegst 2006). The R-values also depend on the moisture content of wood and consequently they were found to be higher in the drier conditions. Regular playing or aging of wood improves the acoustical performance of musical instruments. Humidity and creep play an important role in this. Hunt and Balsan (1996) showed experimentally that regular playing at intermediate or high humidity levels leads to an increase in stiffness (Young's modulus) and a decrease in loss coefficient.

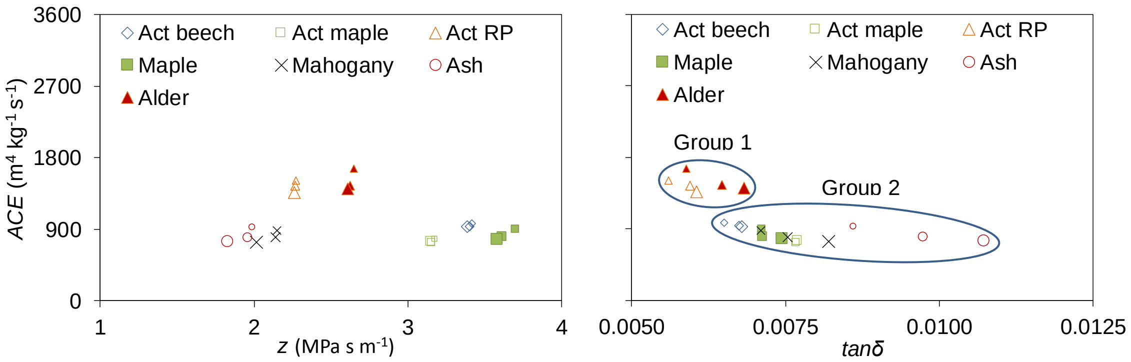

Figure 3: Acoustic conversion efficiency (ACE) plotted against (left) the specific acoustic impedance (z) and (right) the damping coefficient (tanδ) of acetylated and reference wood materials at different relative humidities. Act: acetylated, RP: radiata pine. Dry (35% RH), standard (65% RH) and wet (85% RH) conditions are indicated by small, medium and large markers, respectively

Table 2: Mean values of acoustic conversion efficiency (ACE) of acetylated and reference wood materials at different relative humidity (RH) levels

Type of wood	***ACE* (m^4 kg^{-1} s^{-1})**		
	35% RH	**65% RH**	**85% RH**
Act beech	973.6 b	936.3 b	928.9 b
Act maple	777.4 c	724.3 d	730.5 c
Act RP	1539.9 a	1446.3 a	1365.2 a
Maple	919.7 b	864.8 bc	804.5 bc
Mahogany	901.7 b	769.0 cd	746.9 c
Ash	886.3 bc	759.9 cd	743.8 c
Alder	1566.8 a	1489.6 a	1387.5 a

Act: acetylated, RP: radiata pine, Mean values followed by different letter within a column indicate that there is a significant difference ($P \leq 0.05$) as determined by ANOVA and Duncan's multiple range test

The differences in density are reflected in the specific acoustic impedance, *z* (Figure 3) but not in *ACE* (peak response). The *z* of a material is related to its Young's' modulus and density (see Equation 2). It is an important parameter for string instruments and often a low *z* is required between 1.2 and 3.4 MPa s m^{-1} and high *z*-value is required for percussion instruments such as xylophones so that resonance will be for a longer period of time (Hilde *et al*. 2014, Wegst 2006). Lower values of *z* ensure an easy transmission of vibrations into the air. Wood with very high *z* and very low *ACE* is not very good acoustically. In this experiment, ash and mahogany had the lower *z* values whilst the acetylated radiata pine and alder had the highest *ACE* with moderate *z* values. High values of both factors are beneficial for xylophone bars (Wegst 2006).

When *ACE* values were plotted against *tanδ* values, clearly two groups of wood materials were identified (Figure 3). One group with high value of *ACE* and low *tanδ* included acetylated radiata pine and alder. A high value of *ACE* in wood is required for excellent soundboard (Brémaud 2012). Rest of the samples were in the second group, which showed lower *ACE* value with higher *tanδ*. The *ACE* values of acetylated wood types were compared with the reference samples. It was found that alder and acetylated radiata pine had significantly higher values than the other wood materials at the different humidity levels (Table 2). Acetylated beech and maple had superior or comparable acoustic performance in terms of *ACE* and *tanδ* with the reference materials. Those materials also had a low variation of physical and acoustical properties with increases in relative humidity, and thus showed a good potential for musical instruments making. However, the final choice of wood for a specific instrument mainly depends on its acoustical properties that are relevant for that use.

CONCLUSIONS

1. Acetylated wood showed better hygroscopic behaviour (*EMC* at dry, standard and wet conditions) and dimensional stability (in terms of volumetric shrinkage) compared with common reference wood materials used in musical instruments making.
2. Sound radiation coefficient (*R*), specific acoustic impedance (*z*) and acoustic conversion efficiency (*ACE*) were increased in the dry condition as compared with standard and wet conditions. Damping coefficient or internal friction ($tan\delta$) decreased in dry condition.
3. Acetylated radiata pine had higher *R* values, while all the other materials showed values in acceptable range suitable for specific musical instruments.
4. All the modified wood materials had *z* values within the tolerable range. The *ACE* of alder and acetylated radiata pine had statistically significant higher values than the other wood materials at each humidity condition.
5. *EMC* at the different humid conditions affected the acoustical properties of acetylated wood samples. They performed better in the dry condition when their *EMC* was the lowest.
6. The overall results suggested that acetylated wood is a promising material for different musical instruments manufacturing. However, a final decision for selecting acetylated wood for a specific musical instrument should be based on its relevant acoustical properties.

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Influence on acoustical properties of resonant soundboard material through different processes of thermal modification

David Zerbst[1], Lothar Clauder[2], Dave Olson[3] and Alexander Pfriem[2]

[1]Daimler AG, MBC Research and Development, Benz-Str., D-71063 Sindelfingen
[email: jonas_david.zerbst@daimler.com]
[2]Eberswalde University for Sustainable Development, Schicklerstr.5, D-16225 Eberswalde
[email: Lothar.Clauder@hnee.de; Alexander.Pfriem@hnee.de]
[3]Pacific Rim Tonewoods, 38511 State Route 20, Concrete, WA 98237
[email: deolsonicloud@icloud.com]

Keywords: acoustical properties, guitar soundboards, thermal modification

ABSTRACT

Different processes of thermal modification (TM) were compared by means of vibrational investigations of the modified wood. It was reviewed how the thermal treatment influences the sound properties of Sitka spruce samples for guitar soundboards. Therefor natural frequencies and damping were measured by acoustic resonance analysis. With this data, elastic constants as Youngs modulus in the longitudinal and radial dimension, Resonance-factor, damping and density were calculated or measured. All treatments increased the sound quality of the wood, defined as a higher ratio of stiffness and density. At the same time, some treatments achieved a lower damping. Summarised process no. 2 achieved the best Resonance-factor, due to the combined increased MOE and reduced density values of the modified wood.

INTRODUCTION

Thermal modification (TM) above 150°C causes partial degradations of cell wall components, which are primary hemicelluloses. This effects lower water sorption and improves dimensional stability and biological durability. Previous evaluations of thermal treatments (120-130°C) for musical instruments were assessed as unsuitable (Gadd, d´Arcy 1986). Later, extensive studies with higher temperatures showed clear improvements of the sound quality, especially for resonance soundboards, compared to untreated wood (Pfriem 2006). This work proposed thermal treatments between 180°C and 220°C for an adjustment of better ratio of the modulus of elasticity (MOE) and the density, caused by the density reduction. A mass loss in turn, by not touching the stiffness, evokes a better transmission of the vibration energy – the damping. On the other hand, some results showed that the bending strength decreases with higher grades of modification (Zauer, Pfriem 2010). Several analysis discovered an increasing MOE at relatively mild treatments around 160-180°C (Millet and Gerhards 1972, Kubojima *et al.* 2000, Zauer *et al.* 2016). Wagenführ *et al.* 2005 confirmed that thermal modification gives higher acoustical improvements in good quality resonance material. Embedded in that context in this study high quality material for soundboards was modified by mild treatments at relatively low temperatures (160°-175°) to achieve an improved ratio of stiffness and density and a lower damping. By measuring the acoustical properties before and after the treatments, the different modification processes of three industrial manufacturers and one laboratory scaled system were compared.

EXPERIMENTAL

The investigated four thermal treatment processes represented the state of the art of the different techniques, extant in Europe. Companies in Europe (processes 1, 2 and 3) ran three processes, process 4 and 5 were run in a laboratory scaled system at Eberswalde University for Sustainable Development.
The study was designed by demanding the companies to mildly decrease density and damping, while preserving or even increasing longitudinal and radial MOE. Therefore, a recipe with maximum temperatures around 175°C and temperature maintenance phases of 2-4 hours was chosen for all techniques. In addition to that, a treatment with 160°C and 12 hours maintenance was run at Eberswalde University for sustainable development. This process excludes oxygen to avoid pyrolysis of the wood surface, through a nitrogen atmosphere. The kiln is equipped with four temperature sensors to observe a homogeneous heat distribution. During the treatment, two sensors are placed inside wood boards with the same dimensions compared to the samples and two sensors log the temperature on the wood surface.

The tested material for the vibrational measurements was Sitka Spruce with dimensions of 540x200x30 mm^3. The high quality tonewood with very straight and regular growth was produced by a specialized sawmill and was cut to guitar soundboards with edges accurately parallel to the grain. With each process 11 of these boards were modified. Before the measurements the specimens were stored under normal climate conditions (20°C/65% rH) until they reached equilibrium stage of moisture.

The aim of this study was to analyze the extend of the change of resonance behavior of the modified material afterwards. Thus, a modal analysis (Figure 1) was carried out by exciting the boards with an impact hammer (PCB M086C01) over evenly distributed points in five rows with nine impact points. Every point was hit three times to get an averaged measurement and to reduce occurring inaccuracies when the hammer hit slightly besides the mark. The sample reacts on an elastic deformation with a transient oscillation in its resting form. An acceleration sensor (PCB M352C65) attached to the back of the samples recorded those vibrations. The input – (impact hammer) and output-signal (acceleration sensor) was delivered to a frontend (VibPilot-4) and then delivered to the analyzing software (M+P International, Smart Office Analyzer, Version 4). There the time dependent signals were turned into spectral data. This data gave the frequency response function (FRF), which represented the characteristic, mechanical response behavior of the structure. Amplitude peaks appearing in these spectra were natural vibrations of the system – the resonances or eigenfrequencies. Those were generated from the laws of transversal wave propagation in solids. Every eigenfrequency has a characteristic mode shape with a certain damping. This data were obtained by curve fitting the set of FRF measurements from the 45 impact points (MDOF method). The eigenfrequencies directly refer to the material properties like density, elasticity and the samples geometry. Therefore, elastic constants can be derived from the vibrational behavior. For the identification of the elastic constants in the longitudinal and the radial direction, the eigenfrequencies of the ordinary bending mode shapes were analyzed (Mode 2 and 4). The calculation was made analogue to Zauer *et al.* (2016) and is based on the equations for analytical termination of flexural vibrations of beams (Dankert and Dankert 2013). In the present measurement setup, the samples were hung up with elastic rubber band and small pins. This suspension guaranteed that the structure oscillated freely, which was presumed as boundary condition for the calculation.

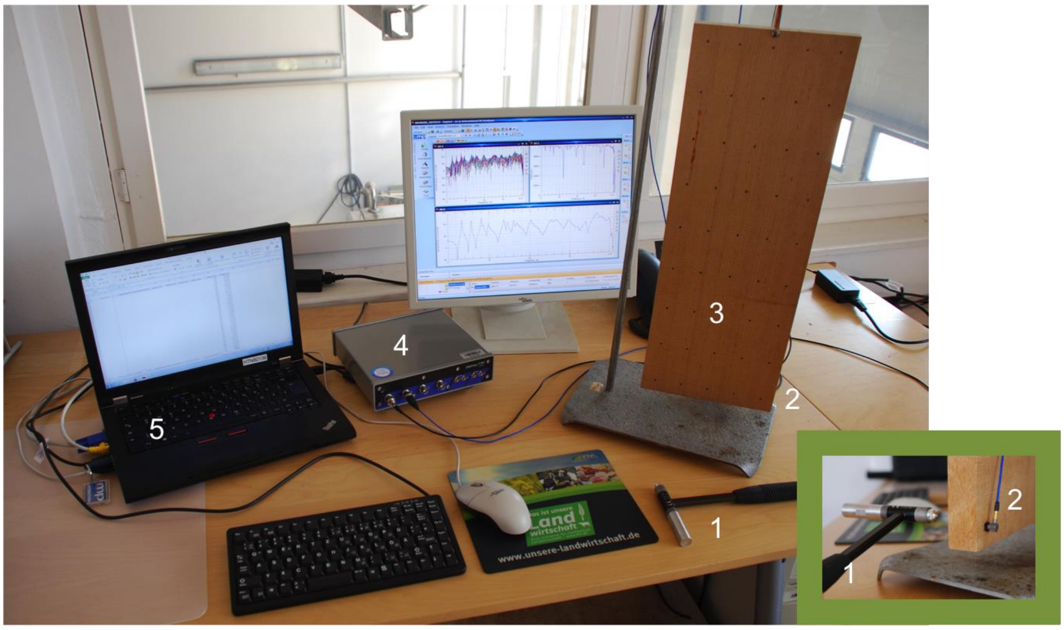

Figure 1: Measurement setup: Impact hammer (1), sensor (2), sample (3) frontend (4), computer (5).

RESULTS AND DISCUSSION

All specimens were stored under standard climate conditions (20°C/65% rH). High quality soundboards require low density and high elastic stiffness. As reference for the Young´s modulus in the longitudinal direction Bucur (2006) gave 13000 N/mm^2 for Sitka Spruce. In this project, a mean longitudinal MOE of 10800 ± 1100 N/mm^2 was calculated. Bucur (2006) indicated the mean density of Sitka spruce with 480 kg/m^3. Density-values of the samples measured in this study varied with 380 ± 30 kg/m^3, at standard climate conditions.

All thermal treatment processes reduced the density of all samples significantly (Figure 2). This reduction was due to the wood mass loss and the reduced sorption capacity. Within a ranking of density reduction, considering that low density causes higher acoustic quality, process no. 5 took first place followed by the processes no. 4, 2, 1 and 3. On the other hand, the samples of the processes no. 4 and 5 (same lab-scale technique) suffered reductions of the MOE due to the treatment (Figure 2), whereby the changes of treatment 4 are not significant under a confidence level of 95%. Significant increase of the MOE was found for the processes 1, 2 and 3. The highest elevation of the stiffness was achieved by treatment process 2.

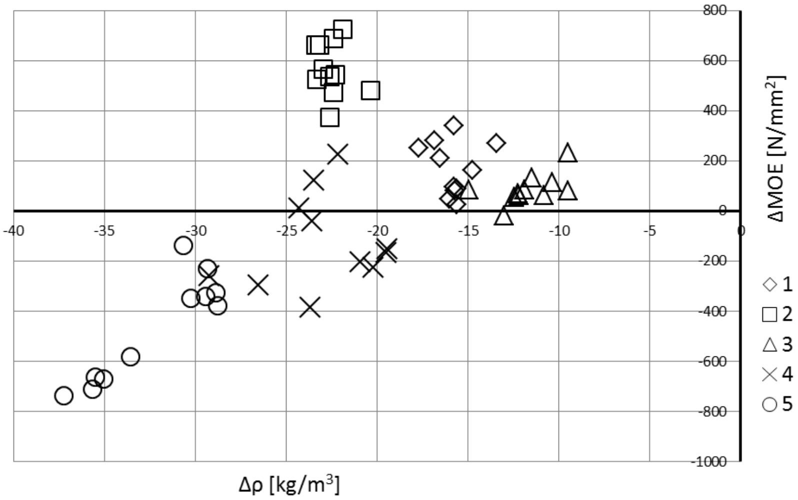

Figure 2: Correlations of change of elastic constants (longitudinal) and density reductions

A further characterisation of acoustic properties was made, by using the Resonance-factor (R-factor), as proposed by Ono *et al.* (1983) and Haines (2000). This factor enabled to predict a good sound quality through a high ratio of sound velocity (c) and density.

$$R = \sqrt{\frac{c}{\rho}} \Leftrightarrow R = \sqrt{\frac{E}{\rho^3}} \qquad (1)$$

Equation 1 shows that especially the density influences this value with the third power under the square root. Thus the R-factor is very highly affected by the treatments (Figures 3 and 4)

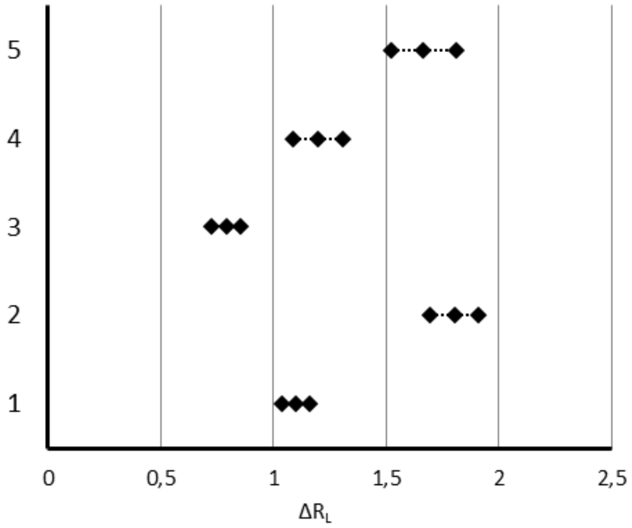

Figure 3: Increases of R-factor (longitudinal) due to the treatments (1 to 5 on y-axis) with means and confidence intervals.

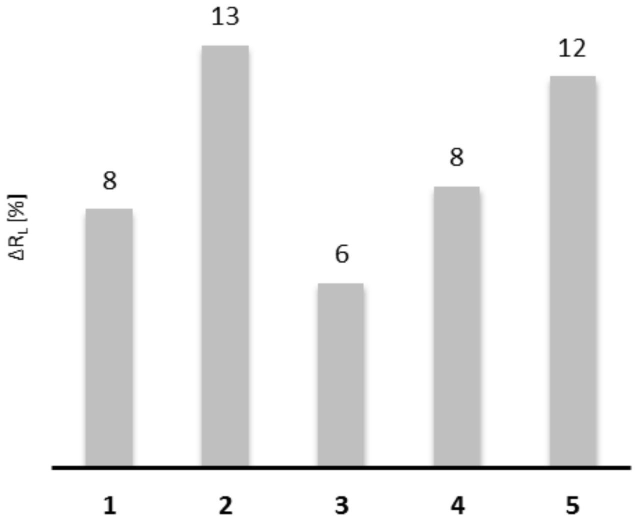

Figure 4: Percentage increases of R-factors (longitudinal) of the different processes 1 to 5

Treatments, which caused higher reductions of density, achieved better R-values. However, to evaluate the sound quality improvements of the different processes based on R, it is assumed that the stiffness of good tonewood should stay stable or even increase, due to the treatment.

Here process 5 achieved very high R, but the high density-reduction went along with a decreased MOE. Summarised process 2 achieved the best Resonance-factor, due to the combined increased MOE and reduced density values.

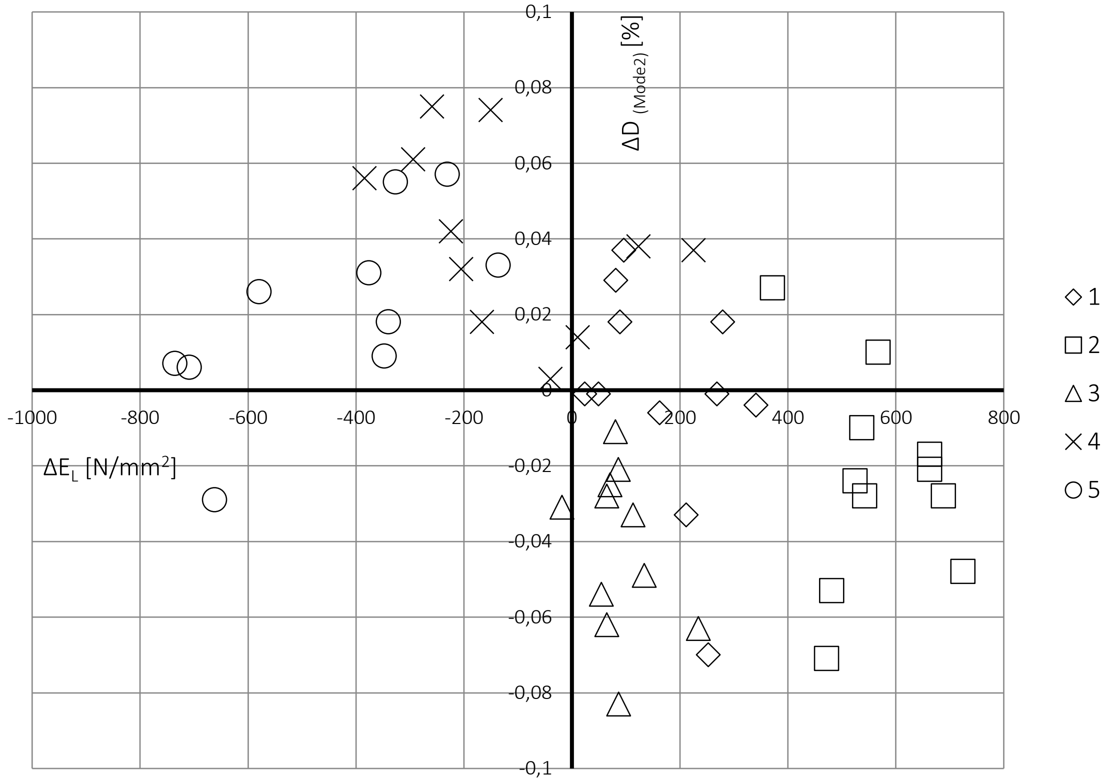

Figure 5: Correlation of change of elastic constants (longitudinal) and damping of mode 2

The damping constants of the first bending modes changed differently for the longitudinal (mode 2, Figure 5) and the radial (mode 4, Figure 6) motion. In general, there were small changes for the damping and the variation was very high, although significant shifts were detected. For a longer sound fade out and a higher reflection of the induced energy at the guitar, a lower damping is requested. For the longitudinal bending mode (Figure 5), this could be achieved from the treatment processes 2 and 3. Process 1 did not change significantly while 4 and 5 increased the damping slightly.

The radial bending vibration was stronger affected (Figure 6). All treatments decreased the damping. The highest reduction of vibration energy absorption was measured on samples of treatment process 3 in both directions. For all samples it could be suggested that there is a weak correlation between the change of the damping and the MOE.

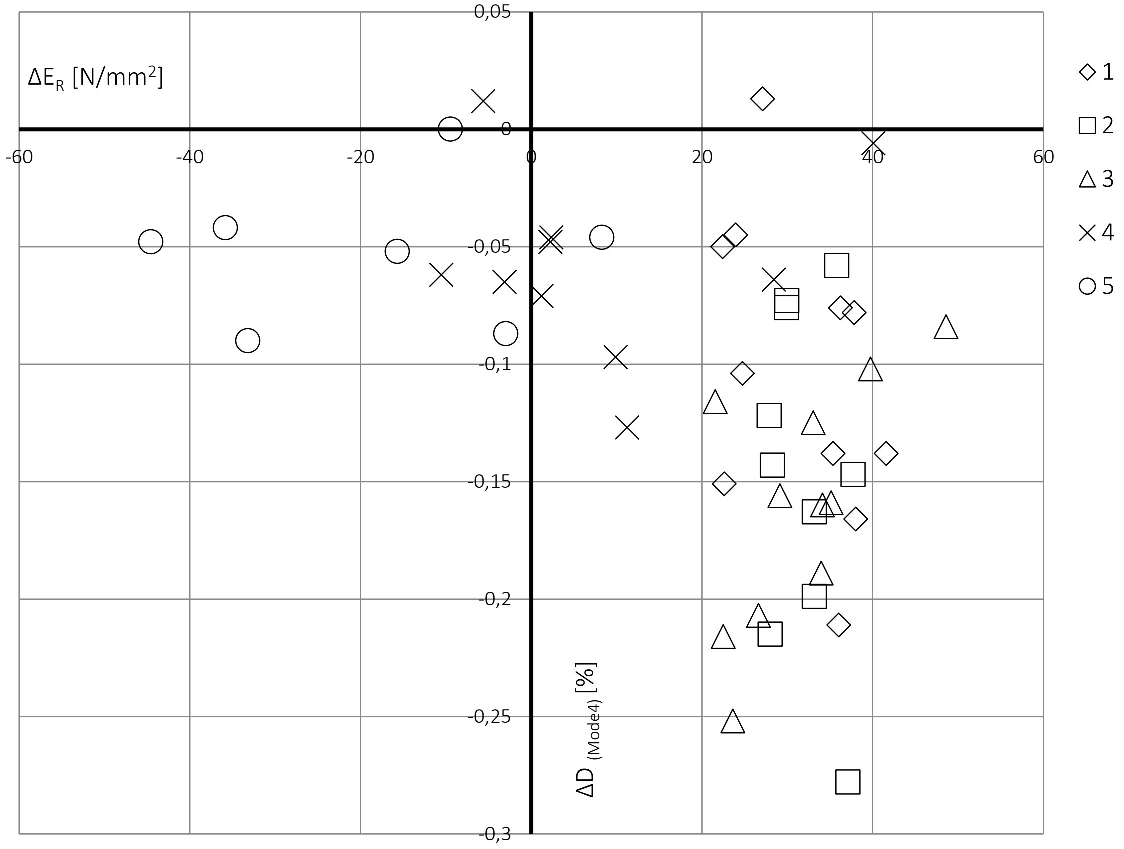

Figure 6: Correlation of change of elastic constants (radial) and damping of mode 4

CONCLUSIONS

Resonant measurements were done before and after thermal treatments from different processes. Due to different techniques and slightly different recipes, all thermal treatments covered a large range of different effects on the resonance behaviour of the samples.

Summarized, an improvement of the sound quality for all of the processes is assumed, considering that some negative effects, like decreased MOE or increasing damping, were rather small. However a classification based on R, like it is done by many previously cited publications, should be perceived with great care. It is obvious that higher degrees of modifications, as found for treatments 4 and 5, gave higher Resonance factors, in respect to the higher influence of the density-values in the Equation 1. For those treatments, the MOE decreased slightly and this work could show that a decreasing stiffness went along with an increase of the damping. These results were confirmed by the fact, that treatment 3 caused the lowest modification degree, regarding the changes of density and MOE and the mass loss, but achieved the highest decrease of the damping. These findings suggest, that a lower degree of modification is preferable for sound quality improvements. The measurements showed clearly the superiority of process 2 in low temperature modification. This treatment exactly matched the desired target between maximum density reduction, maximum MOE increase and damping reduction. The other processes delivered either good damping reductions without changing the MOE or higher density reduction but a weakening of the MOE.

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Measuring the Free Hydroxyl Content in Wood Modified by Acetic or Propionic Anhydride

Callum Hill[1,3], Greeley Beck[1], Erik Larnøy[1], Sarah Strohbusch[2], Holger Militz[2]

[1]NIBIO, As, Norway [email: enquiries@jchindustrial.co.uk]
[2]University of Göttingen, Göttingen, Germany
[3]JCH Industrial Ecology Ltd, Bangor, Gwynedd, UK

Keywords: Acetylation, deuterium exchange, hydroxyl groups, propionylation, saponification

ABSTRACT

Previous studies of the reaction of wood with acetic anhydride have invariably relied upon the use of weight percentage gain (WPG) as a measure of degree of substitution of OH groups in the wood. It is usually assumed that WPG is correlated with the number of OH groups substituted, but this cannot be assumed, since loss of leachable material from the wood during the acetylation reaction will obviously result in weight loss. Saponification followed by an assay procedure (such as HPLC) can be used to measure the amount of acetyl bound in the wood, which can be a reliable method provided (a) the saponification does remove all of the bound acetyl, (b) there is no residual acetic acid in the wood that is physisorbed in the wood substance. Another approach is to use deuterium exchange, where the wood sample is exposed in an atmosphere of deuterium oxide and sufficient time allowed for the deuterium atoms to exchange with the hydrogen atoms in the accessible OH groups of the wood. This method has been previously applied to acetylated wood previously using a dynamic vapour sorption apparatus. The results from this study showed that there was a slightly lower accessible OH content than was calculated theoretically. This was thought to be due to loss of thermally labile materials from the wood during the acetylation process, but could also suggest some steric ‘masking’ of adjacent OH groups by the bonded acetyl groups. It was not possible to decide which of these mechanisms was operative, since no independent measure of the bound acetyl content was undertaken. The present study was initiated to remedy the deficiencies of the previous study by directly measuring the acetyl content, in addition to measuring the accessible OH content using deuterium exchange. Furthermore, a separate set of experiments was undertaken by using modification of wood with propionic anhydride. By using two different anhydrides of different molecular weight it is possible to have different levels of OH substitution at the same WPG. Saponification of the acetylated wood followed published procedures, but it was found that the published method did not remove all of the bound acetyl and the procedure was accordingly modified. The results obtained suggest that the reduction in OH content due to acetylation was not solely due to substitution of the free OH content, but there was also some ‘masking’ of adjacent OH groups. Meanwhile, the propionic anhydride modified wood showed evidence for some cell wall degradation creating additional OH groups during the procedure.

INTRODUCTION

Acetylation of wood involves the substitution of the cell wall polymer hydroxyl (OH) groups with acetyl moieties, which leads to improved dimensional stability and decay resistance (Kumar 1994, Rowell 2005, Hill 2007, Thybring 2013). The substitution reduces the number of OH groups available for hydrogen bonding to water molecules and also bulks the wood cell wall, taking up physical space within the nanostructure, thereby reducing the volume available to water.

Moisture exclusion within the acetylated cell wall may be due to OH substitution, physical bulking (i.e., moisture exclusion) or a combination of the two. Thygesen and Elder (2008) used time-domain NMR to characterise water in acetylated wood. They found slightly reduced relaxation time for the cell wall water population and they attributed this to cell wall bulking. Papadopoulos and Hill (2003) investigated the mechanism behind reduced moisture sorption in acetylated wood by modifying wood samples with a series of linear chain anhydrides. By increasing the length of the linear carbon chain attached at the ester bond formed during the modification, the authors obtained various levels of OH substitution at equivalent weight percentage gains (WPG). The results from this study showed that reduction in equilibrium moisture content was approximately similar for samples of similar WPG, regardless of degree of OH substitution. However, the measure of OH accessibility used in their study was an indirect measure based on weight gain only. Furthermore, the WPG was assumed to be directly related to the acetyl content.

Accessible OH content in acetylated wood was directly determined by Popescu *et al*. (2014) using deuterium exchange in a dynamic vapour sorption (DVS) apparatus. The theory behind this technique was originally proposed for measuring OH accessibility in cellulose in the 1960's (Morrison 1960, Sepall and Mason 1961). When a hygroscopic sample is continually exposed to deuterium oxide (D2O), protons in the accessible OH groups are exchanged for deuterons. This increases the mass of the sample and that mass change is detectable with an extremely sensitive balance, such as the one in a DVS apparatus. This method has recently been used to determine OH accessibility in thermally modified wood (Rautkari *et al*. 2013), birch craft pulps (Pönni *et al*. 2014), torrefied wood and charcoal (Kymäläinen *et al*. 2015) and green wood after drying and re-wetting procedures (Thybring *et al*. 2017). When Popescu et al. (2014) employed the technique on acetylated wood, they found that reduction in OH accessibility due to acetylation correlated well with WPG. The authors also calculated theoretical OH content in the acetylated samples by dividing the mass change due to acetylation by the molar mass of the acetyl group and subtracting this value from the average accessible OH content of the unmodified samples. The relationship between accessibility and WPG determined experimentally, differed from this theoretical relationship. However, in their study, the acetyl content was not directly measured and it was assumed that it was proportional to the WPG. To further examine this apparent disagreement, the bound acetyl content in the acetylated samples should be directly measured to see if the number of added acetyl groups accounts for the number of inaccessible hydroxyl groups. One way of determining bound acetyl content is through saponification of the ester bond by sodium hydroxide (NaOH) and subsequent analysis of the acetic acid product (Rowell *et al*. 1994, ICC Evaluation Services, Inc. 2005). In the study reported herein, OH accessibility in acetylated samples was measured by deuterium exchange and was compared with the theoretically obtained value, as well as the bound acetyl content determined through saponification. Such a study has not been previously performed before on acetylated wood. Additionally, this work further investigates the mechanism behind moisture exclusion in acetylated wood by performing the deuterium exchange experiment on samples reacted with propionic anhydride. Similar to Papadopoulos and Hill (2003), the longer carbon chain in the propionic anhydride will result in lower OH substitution in the reacted wood at equivalent levels of WPG when compared to acetylated samples. However, Papadopoulos and Hill (2003) indirectly determined OH content from weight gain, whereas the deuterium exchange experiment provides a direct measure of OH accessibility and allows the relationship between weight gain and OH content to be explored directly. Saponification was also used to directly measure the propionyl content of the modified wood. Measurements of OH accessibility with deuterium exchange have recently been performed using a DVS apparatus (Rautkari *et al*. 2013, Popescu *et al*. 2014, Pönni *et al*. 2014, Kymäläinen *et al*. 2015, Thybring *et al*. 2017). However, since the experiment only requires an extremely sensitive balance in a closely controlled humidity atmosphere, equipment designed for thermogravimetric analysis

(TGA) can also meet these conditions. In this paper, deuterium exchange was performed on a modified TGA instrument.

MATERIALS AND METHODS

Materials

A single *Pinus radiata* (D. Don) sapwood board was initially cut in the transverse plane to produce 1 cm thick slices. Cylinders 0.6 cm in diameter were then punched out of the earlywood portion of the growth rings with a steel hole punch so that the cylinder length was oriented along the fibre direction. These small dowels (1 cm length, 0.6 cm diameter) were labelled and then extracted with acetone for six hours in a 250 ml Soxhlet apparatus with single coil condenser. After this initial extraction, the samples were dried for 18 hours at 103°C and weighed to obtain an unreacted dry weight. The samples were then submerged in room temperature acetic anhydride or propionic anhydride and weighed down under plastic netting. While submerged, the samples were vacuum impregnated using 0.02 bar pressure for 2 hours. The vacuum was then released and the samples soaked in the anhydride for 24 hours. The impregnated samples were then added to a preheated reaction flask in an oil bath at 110°C containing 500 ml of the corresponding anhydride solution. Various reaction times were used to obtain a range of WPG values. Because the reaction kinetics for the propionic anhydride modification proceed slower than acetylation (Hill and Jones 1996, Hill *et al*. 1998), the propionylated samples were accordingly reacted for longer periods to obtain comparable levels of reaction. The heated anhydride was then poured out and 250 ml of room temperature acetone was added to the flask to quench the reaction. In order to remove the acid by-product and residual anhydride, the samples were extracted again in the same Soxhlet apparatus using a fresh mixture of toluene/acetone/methanol (4:1:1, v/v) for 6 hours. The reacted and extracted samples were then dried for 18 hours at 103°C and weighed to determine WPG. The same extractions and drying periods were used on the unmodified control samples, but they were not reacted with anhydride. Initially, three modified dowels with various WPG values were selected for each modification type to be used in further analyses. Later, an additional three acetylated dowels were selected to replace the first set for saponification analysis. The small dowels were divided into approximately 1-2 mm circular sections by sawing them in the transverse direction. The sections were then cut with a razor blade and reduced in size until their weight was between 5.9 – 6.1 mg (un-dried mass). These 6 mg samples were then used for the deuterium exchange experiment.

Deuterium exchange

Hydroxyl accessibility was quantified by measuring mass increase due to deuterium exchange in a Pyris 1 Thermogravimetric Analyser (PerkinElmer, USA) with a measuring accuracy of 0.1 μg. Samples weighing approximately 6 mg were placed in open instrument crucibles and hung from the microbalance wire. Each sample was initially dried using dry nitrogen gas (flow rate 50 ml min-1) and a chamber temperature of 103°C for 30 minutes. The temperature was then reduced to 25°C and the sample was held in the dry nitrogen environment for another 115 minutes. Next, the gas flow was switched to D_2O vapour (50 ml min-1) and the sample was conditioned in a near saturation D_2O environment for 360 minutes. The conditioning period was followed by another drying step using dry nitrogen at 103°C for 30 minutes. Finally, the temperature was decreased to 25 °C, maintaining the dry nitrogen environment, and held for another 115 minutes. Hydroxyl accessibility was calculated as in Popescu *et al*. (2014) where the added mass due to chemical modification is accounted for by determining OH accessibility on a dry, unreacted wood mass basis. Dry masses before and after D_2O conditioning were calculated by averaging the values in the last 10 minutes of each 25°C dry nitrogen period. The accessible OH content was then determined as in (Pönni *et al*. (2014). Theoretical OH content was also determined for the acetylated samples as in Popescu *et al*. (2014) by dividing the mass change due to acetylation by 42.037 g mol^{-1} (molar mass of acetyl group - molar mass of hydrogen) and subtracting this value from the average accessible OH content calculated from deuterium exchange for the unmodified wood samples. The same calculation was done for the propionylated samples, but the mass change due to modification was divided by 56.064 g mol^{-1} (molar mass of propionyl group - molar mass of hydrogen).

Bound acetyl content

After the deuterium exchange measurement, the samples were analysed for bound acetyl/propionyl content (on an unreacted wood mass basis) using saponification methods based on ICC Evaluation Services, Inc. 'Acceptance Criteria for Acetylated Wood Preservative Systems' (2005). To the authors' knowledge, no peer reviewed literature describes method details for saponification of acetylated wood, so the ICC Evaluation Services, Inc. technique was used to begin with. One set of acetylated samples was initially analysed using the 2-hour saponification time specified in this method. To determine the saponification time necessary to release the bound propionyl groups, additional highly propionylated samples (WPG > 20%) were measured after various saponification reaction times to determine a release curve. Additional highly acetylated samples were also included in this time series experiment to check that two hours specified in the aforementioned method were sufficient for complete bound acetyl release. Each 6 mg sample was placed in a 2 ml Eppendorf tube and 240 µl of 1 M NaOH was added. The tubes were placed on a shake table and 100 µl of the solution was pipetted out after different time periods for HPLC analysis with one sample dedicated to each time point. The sample solutions were then mixed with 100 µl of 0.2 M phosphate buffer in HPLC vials and loaded into the instrument. The analysis was performed on an Agilent Series 1100 HPLC with a diode array detector (Agilent Technologies, Palo Alto, CA, USA). The mobile phase was 20 mM sulphuric acid (flow rate 0.6 ml/min). An Aminex HPX-87H column (Bio-Rad, Hercules, CA, USA) was used at 30°C with an injection volume of 20 µl per sample and the detection mode was UV (210 nm). Standard curves were made for both acetic acid and propionic acid using six samples of known concentration and from these standard curves the exact concentration of acetic or propionic acid in each HPLC sample was determined. This concentration was doubled to account for the dilution with the phosphate buffer and then multiplied by 240 µl to determine the amount of acetic or propionic acid resulting from saponification. Because each acetyl or propionyl group is converted to its corresponding acid by saponification, this amount is equivalent to the bound acetyl or propionyl content in the wood. The saponification reaction time determined from the release curves were then used for the propionylated samples measured with deuterium exchange and for the second set of acetylated samples. The HPLC procedure used for these samples was the same as that described for the release curve. The values determined for acetylated samples were then adjusted to account for the naturally occurring acetyl content in the wood by subtracting the average bound acetyl content of unmodified samples from the acetylated values. Unmodified samples had no detectable bound propionyl content so this adjustment was not necessary for propionylated samples. Theoretical bound acetyl and propionyl content on an unreacted wood mass basis were also determined by dividing the mass change from the modification by 42.037 g mol^{-1} or 56.064 g mol^{-1} (molar mass of acetyl or propionyl group - molar mass of hydrogen). Lastly, OH accessibility values determined from deuterium exchange were used to calculate bound acetyl or propionyl content, by assuming that all reduction in OH accessibility results from the substitution of an OH group with an acetyl or propionyl group. Thus, bound acetyl or propionyl content was calculated by subtracting the OH accessibility of the modified sample from the average OH accessibility of the unmodified samples.

RESULTS AND DISCUSSION

When deuterium exchange experiments have previously been performed in a DVS apparatus, deuterium conditioning is typically done by cycling the material through multiple wetting and drying periods (Lee *et al*. 2011, Popescu *et al*. 2014, Pönni *et al*. 2014, Kymäläinen *et al*. 2015). However, deuterium exchange has been shown to depend only on the length of deuterium conditioning time, not the number of cycles, for both cellulose (Pönni et al. 2014) and wood (Rautkari et al. 2013). Therefore, only one deuterium conditioning period was used in the exchange experiments. The exact relative humidity during D_2O conditioning was not measured, but the vapour was near saturation, well above the critical 60% relative humidity level, over which no further deuteration occurs (Taniguchi 1978). The length of the conditioning period was tested by comparing three unmodified samples conditioned for 360 minutes to three samples conditioned for 720 minutes and no significant difference in mass change was found. Thus, 360 minutes was determined to be sufficient to achieve full deuteration for the instrument used here. However, there may be some small error in these measurements, as other studies employing DVS apparatus for deuterium exchange in wood have used somewhat longer conditioning periods (Rautkari *et al*. 2013, Popescu *et al*. 2014, Thybring *et al*. 2017). The 30-minute, heating step at 103°C used initially in the drying periods was to facilitate water removal and accelerate the drying process. Thermal degradation of wood during such a short heating period at this temperature is essentially negligible (Stamm 1956).

The accessibility of OH groups of unmodified, acetylated and propionylated samples are presented in Figure 1. The average accessibility of the six untreated samples was 9.0 mmol g^{-1} which agrees with literature values (Rautkari *et al*. 2013, Popescu *et al*. 2014, Kymäläinen *et al*. 2015). As expected, higher levels of acetylation showed decreased hydroxyl accessibility. However, the effect of acetylation on OH accessibility deviated from the theoretical relationship calculated from weight gain (shown by the black blue line). The experimentally determined accessibilities were consistently lower than the theoretical values, similar to results from Popescu *et al*. (2014). This suggests that, in addition to OH substitution, acetylation may further reduce OH accessibility by hindering access to unmodified OH groups. However, as Popescu *et al*. (2014) point out, WPG values calculated for the samples may underestimate bound acetyl content due to the loss of thermally labile cell wall components as the reaction proceeds. This would mean that the WPG due to added acetyl groups is actually higher than values determined from post-reaction weight. Therefore, these results alone are not sufficient to conclude that physical hindrance of unmodified OH groups plays a role in OH accessibility reduction in acetylated wood.

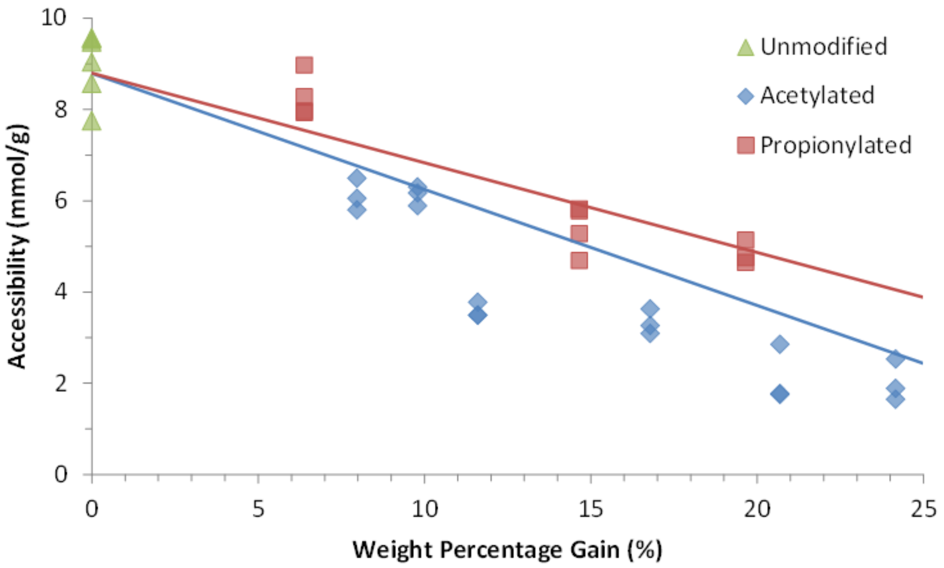

Figure 1: Hydroxyl accessibility per gram of wood material as a function of weight percentage gain for unmodified, acetylated and propionylated Pinus radiata earlywood determined experimentally using deuterium exchange and also calculated theoretically (blue line for acetylation and red line for propionylation).

Propionylation also reduced OH accessibility at the two higher WPG values, but the lowest WPG samples did not reduce accessibility compared to the unmodified samples (Fig. 2). These low WPG samples actually had higher values than theoretically predicted (grey red line) and contradict the expectation that substitution of hydroxyl groups with propionyl groups will decrease accessibility. One possible explanation is that, in addition to replacing OH groups, the propionylation reaction may also cause internal stresses which open up the cell wall structure and expose new hydroxyls. This would have the effect of increasing accessible OH content and potentially compensate for the reduction due to OH substitution. Rautkari *et al*. (2013) showed that the OH accessibility of acacia wood measured by deuterium exchange, increased when the wood was thermally modified at 180°C for two hours, perhaps also due to structural changes in the cell wall. The randomness of this process may also explain the observed large variation in WPG for samples reacted with propionic anhydride for the same amount of time. All the propionylated samples selected to be used in this study were reacted for 500 minutes, giving a range of WPG values from 6 to 20%. Hill and Jones (1996) also obtained widely variable WPG values for propionylated Corsican pine samples reacted with a pyridine catalyst at 110 °C. The increase in accessibility which compensates for substituted hydroxyls is only present in the low WPG propionylated samples. At the two higher WPG values, the experimental measurements seem to agree with the theoretical relationship, supporting the substitution theory. However, it is likely that the molecular structure of the cell wall has also been rearranged in these high WPG samples, increasing OH accessibility. Unfortunately, it is not possible to determine the effect of propionylation in isolation from these results, because the extent of OH accessibility increase due to molecular restructuring is unknown.

CONCLUSIONS

The deuterium exchange experiment was successfully performed in an instrument designed for thermogravimetric analysis. Hydroxyl accessibility results for unmodified and acetylated samples agree with results published in the literature where experiments have been performed in a DVS apparatus. For acetylated samples, the combination of hydroxyl accessibility data obtained from deuterium exchange and bound acetyl content determined with saponification provides strong evidence that steric hindrance plays a role in limiting access of water to unmodified hydroxyl groups. Saponification results also indicate that WPG tends to underestimate bound acetyl content. Results for propionylated samples suggest that the propionylation reaction damages the cell wall, restructuring polymers such that new hydroxyl groups become exposed. This cell wall damage makes comparison between propionylated and acetylated samples difficult, but if an adjustment is made to propionylated accessibility values based on an estimate of hydroxyl accessibility increase due to cell wall damage, results seem to confirm that there is some steric hindrance of hydroxyl groups.

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Pre-treatment with Ionic Liquids or Organic Superbases to Reduce the Spring-Back and Set-Recovery of Surface-Densified Scots Pine

Benedikt Neyses[1], Olov Karlsson[2] and Dick Sandberg[3]

[1]Luleå University of Technology, Forskargatan 1, SE-93187, Skellefteå [email: benedikt.neyses@ltu.se]
[2] Luleå University of Technology, Forskargatan 1, SE-93187, Skellefteå [email: olov.karlsson@ltu.se]
[3] Luleå University of Technology, Forskargatan 1, SE-93187, Skellefteå [email: dick.sandberg@ltu.se]

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ABSTRACT

Compressing the surface of a wooden board results in a layer of densified wood cells a few millimetres thick and a substantial increase in hardness. Surface densification of soft woods such as Scots pine opens up new market opportunities for high-value wood products, but wide-spread commercialisation is unfortunately hindered by the lack of an industrially viable densification process, the major obstacle being the recovery of the densified wood cells upon exposure to moisture. This so-called set-recovery is due to insufficient plastic deformation of the crystalline cellulose, which is kept in a meta-stable state by the surrounding hemicellulose and lignin matrix. In recent years, the dissolution of cellulose in ionic liquids became increasingly popular. These ionic liquids are primarily based on imidazolium rings or on mixtures of an organic superbase and a carboxylic acid. Our hypothesis is that partial dissolution of the crystalline cellulose will largely prevent the set-recovery of densified wood, and the objective of this study was to evaluate the effect of ionic liquid and superbase pre-treatment on the elastic spring-back and set-recovery of surface-densified wood. Specimens of Scots pine (*Pinus sylvestris* L.) were treated with ionic liquids or superbases diluted in ethanol, and then densified in a hot press at temperatures between 200°C and 270°C. The set-recovery was measured after one and two wet-dry cycles. The spring-back when the press was opened was completely eliminated. Depending on the pressing temperature, the set-recovery could be reduced from about 90% for the control group to only about 10% for the chemically treated specimens. A positive correlation between the reduction in set-recovery and the concentration of the chemical solution was also observed. The treatment and densification process presented in this study can be seen as a precursor to the development of a continuous densification process. A closed system is not necessary and both the chemical treatment and the densification stage have the potential to be performed in a continuous manner. Further studies are however needed to optimize the treatment and understand its underlying mechanisms.

INTRODUCTION

Although it is not a new research area in the field of wood science, the surface densification of wooden boards has in recent years been a subject of increasing popularity. Creating a layer of densified wood cells a few millimetres thick just beneath the surface can lead to a twofold increase in hardness (Gong *et al.* 2010, Laine *et al.* 2013), and this opens up new opportunities for low-density woods species to be used for high value products, such as wooden flooring or window frames.

One of the major obstacles preventing the widespread commercialisation of surface-densified wood products is the elastic spring-back and in particular the set-recovery of the compressed wood cells in the context of an industrial process. The elastic spring-back – which occurs immediately when releasing the compression force – is greatly reduced by introducing a cooling stage before the pressure is released at the end of the densification process (Neyses 2016), and the moisture-induced set-recovery can be eliminated by chemical modification, by impregnation, or by a thermo-hydro-mechanical post-treatment stage (Kutnar *et al.* 2015). These established methods are however either very time-consuming or difficult to translate into a continuous process.

One of the major theories describing the underlying mechanisms of the elastic spring-back and the set-recovery was presented by Navi and Sandberg (2012) and further described by Navi and Pizzi (2014), who suggested that the set-recovery is due to the elastic deformation of crystalline cellulose, which is 'frozen' inside the plastically deformed matrix of lignin and hemicellulose. A re-plasticisation of the matrix after it has been densified, e.g. through moisture, leads to a recovery of the elastic deformation in the crystalline cellulose. Our hypothesis is that the set-recovery will be greatly reduced if a plastic deformation of the crystalline cellulose can be achieved in the initial plasticisation stage before densification. This is, however, difficult to accomplish with the existing methods of plasticising wood, such as the combination of moisture and heat, or treatment with gaseous ammonia.

Starting in the 21st century, several studies have explored the possibility of plasticising cellulose by treatment with so-called *ionic liquids* (ILs) (Swatloski *et al.* 2002, Kilpeläinen *et al.* 2007). An IL is a salt that is liquid at relatively low temperatures, normally below 100°C, and consists of ions instead of electrically neutral molecules. Apart from being considered to be *green solvents* of cellulose, ILs are reported to have antifungal and antimicrobial effects, and increase the fire resistance and UV-stability of wood. Ou *et al.* (2014) reported that IL treatment transforms wood into a thermoplastic material with only a very small elastic deformation under load. This behaviour suggests that the elastic spring-back and the set-recovery can be largely reduced by such treatment. The first generation of ILs that were used to dissolve cellulose consist of imidazolium-based cations, often combined with a halogen anion, such as chloride or bromide. These ILs are highly effective, but also expensive. More recently, several studies have explored the potential of ILs made of amidine- or guanidine-based cations, combined with a carboxylic acid, such as propionic acid or acetic acid as the anion (King *et al.* 2011). Due to their high basicity, these amidines and guanidines are also known as *superbases* (Ishikawa 2009). Parviainen *et al.* (2013) and Hanabusa *et al.* (2018) reported that this new generation of ILs is considerably cheaper and easier to recycle than imidazolium-based ILs. As wood is itself somewhat acidic, we also decided to test a pre-treatment with only the amidine or guanidine component as cations, to see whether they would form an IL in-situ with the wood's acid groups as the anions. The in-situ IL would then plasticise the cellulose.

The purpose of this study was to evaluate the effect of ionic liquid and superbase pre-treatments on the elastic spring-back and the set-recovery of surface-densified wood, and we therefore screened various combinations of chemical compounds, solution concentrations and densification temperatures.

EXPERIMENTAL

Specimen preparation

The study was carried out on knot-free sapwood specimens of Scots pine (*Pinus sylvestris* L.) with dimensions of 124 mm (L) x 25 mm (T) x 18.5 mm (R). The annual ring orientation was within ±15° parallel to the tangential wood surface to be densified. The specimens were kept in a climate chamber at a temperature of 20°C and 65% relative humidity (RH) until they reached the equilibrium moisture content (MC).

Preparation of chemicals

The specimens were treated with various ILs or organic superbases, diluted with ethanol to different concentrations (Table 1). The IL 1-Butyl-3-methylimidazolium chloride (Bmim[Cl]), and the superbases 1,5-Diazabicyclo(4.3.0)non-5-ene (DBN), 1,8-Diazabicyclo(5.4.0)undec-7-ene (DBU) and 1,1,3,3-Tetramethylguanidine (TMG) were purchased from Acros Organics. Another IL was made by mixing DBN with propionic acid in an equimolar ratio, resulting in DBN propionate (DBN[$EtCO_2H$]).

Chemical pre-treatment

Prior to densification, the chemical solutions were applied with a pipette onto the wood surface to be densified. In order to keep the amount of solution consistent, the content of one pipette filling was distributed over the surfaces of two specimens. Within one minute, the solutions were completely soaked up by the wood. This procedure was repeated three more times for each specimen. In order to encourage the penetration of the chemicals into the wood surface, the surfaces were punctured with 3-4 mm deep holes with a diameter of about 0.8 mm. Only group 250NDBU (Table 1) was left without holes. All specimen groups to be chemically treated were oven dried at 103°C to an MC of 0% prior to the pre-treatment. After the pre-treatment, the specimens were kept in an oven at a temperature of 60°C for 14 hours to evaporate the ethanol.

Densification process

The specimens were densified in the radial direction on the sapwood side in a hot press with a water-cooling system. Two or three specimens were densified at the same time. For the first 10 seconds of the process, only a low pressure was applied, enough to maintain proper contact between the wood surfaces and the heated press platen. The pressure was then increased to a level that would only lead to densification if the wood cells were sufficiently plasticised. Depending on the parameters and the treatment, the target thickness of 15 mm (set by metal stops in the press) was achieved after a time between 90 s and 240 s (Table 1). Regardless of the time taken to reach the target compression, the specimens were kept at the set temperature for a total of 240 s, after which the cooling system was started. The press was opened when the press platen temperature reached 60°C. After the densification process, all the specimens were kept in an oven at 60°C before the set-recovery was determined.

Specimen grouping

Table 1 lists the specimen groups with their respective treatments and densification parameters.

Table 1: Overview of the specimen groups: CE – Concentration in ethanol, T - Press-platen temperature; P – Densification pressure; t1 - Time to reach target thickness; t2 - Total time in press before cooling

Group	Chemical pre-treatment	CE [wt%]	T [°C]	MC [%]	P [MPa]	t1 [s]	t2 [s]
C150	-	-	150	14.8	3.5	80	90
R270	-	-	270	14.8	3.5	80	330
R250	-	-	250	14.8	3.5	80	330
R230	-	-	230	14.8	3.5	80	330
R200	-	-	200	14.8	3.5	80	330
270BMIM	BMIM[Cl]	20	270	0	3.2	90	240
270DBNIL	DBN[EtCO$_2$H]	20	270	0	3.2	90	240
270DBN	DBN	20	270	0	3.2	90	240
270TMG	TMG	20	270	0	3.2	90	240
270DBU	DBU	20	270	0	3.2	90	240
250DBU	DBU	20	250	0	3.2	120	240
230DBU	DBU	20	230	0	3.5	150	240
200DBU	DBU	20	200	0	4.4	230	240
250HDBU	DBU	30	250	0	3.2	120	240
250LDBU	DBU	10	250	0	3.2	170	240
250WDBU	DBU	20	250	5	3.2	120	240
250NDBU	DBU	20	250	0	3.2	120	240

Group C150 is the control group, densified with parameters similar to those used in existing surface densification procedures. The purpose of groups R270-200 was to separate the effect of thermal treatment from the effect of the chemical pre-treatment on the spring-back and set-recovery. After being densified with the same parameters as group C150, these four groups were put back in the press for 240 s at temperatures between 270°C and 200°C. The chosen temperatures correspond to the densification temperatures of the chemically pre-treated specimens.

Group C150 consisted of 6 specimens, groups R270-200 had 5 specimens each, and the remaining groups consisted of 10 specimens. The average oven-dry density of each group was between 432 and 450 kg/m^3.

Elastic spring-back

The elastic spring-back (SB) is defined as:

$$\mathrm{SB}\ (\%) = (B'_c - B_c)/(B_0 - B_c) \tag{1}$$

where B_0 is the thickness of the specimen before densification, B_c is the target thickness of the specimens after densification (15 mm) and B'_c is the actual thickness of the specimens after densification. The spring-back can thus vary between 0% and 100%, where 0% indicates no spring-back and 100% indicates full spring-back.

Set-recovery

The set-recovery measurements were carried out on pieces with a length of 15 mm cut from the densified specimens, which were measured with a digital calliper after one and two cycles of soaking in water for at least 14 h at room temperature, followed by oven-drying at 60°C for 24 h. The set-recovery (SR) is defined as:

$$\mathrm{SR}\ (\%) = (R'_c - R_c)/(R_0 - R_c) \tag{2}$$

where R_0 is the oven-dry thickness of the specimen before densification, R_c is the thickness of the specimen after densification and R'_c is the thickness of the densified specimen after the wet-dry cycling. The set-recovery can vary between 0% and 100%, where 0% indicates that there is no shape memory, i.e. that the compression-set is completely fixed, and where 100% indicates that the recovery is total. After the first wet-dry cycle the specimens exhibited cupping of the densified surface, and in this case the average value of the maximum and minimum thickness of each specimen was used for R'_c.

There was a problem in this way of calculating the set-recovery because the initial, uncompressed oven-dry thickness was not known for the specimens that were densified at an MC of 14.8% or 5%. In this case the oven-dry thickness of the specimens was assumed to be equal to the average thickness of all the specimens densified at an MC of 0%.

RESULTS AND DISCUSSION

The effect of a pre-treatment with ionic liquids (ILs) or organic superbases on the elastic spring-back and the set-recovery of surface-densified wood was studied. It has been reported that the spring-back of untreated surface-densified Scots pine wood is about 50% without a cooling stage (Neyses *et al.* 2017), and about 10% with a cooling stage, and this has been verified in the present study (group C150) (Laine *et al.* 2013, and Neyses *et al.* 2017).

For all other groups, with the exception of group 200DBU the spring-back was negligible within the accuracy of the measurement device. Group 200DBU had on average 5% spring-back. This level of spring-back was due to the fact that these specimens never reached the target thickness. It is suggested that the low moisture content of the chemically treated specimens prevents unwanted elastic deformation of the wood cells, and this results in a complete elimination of the spring-back.

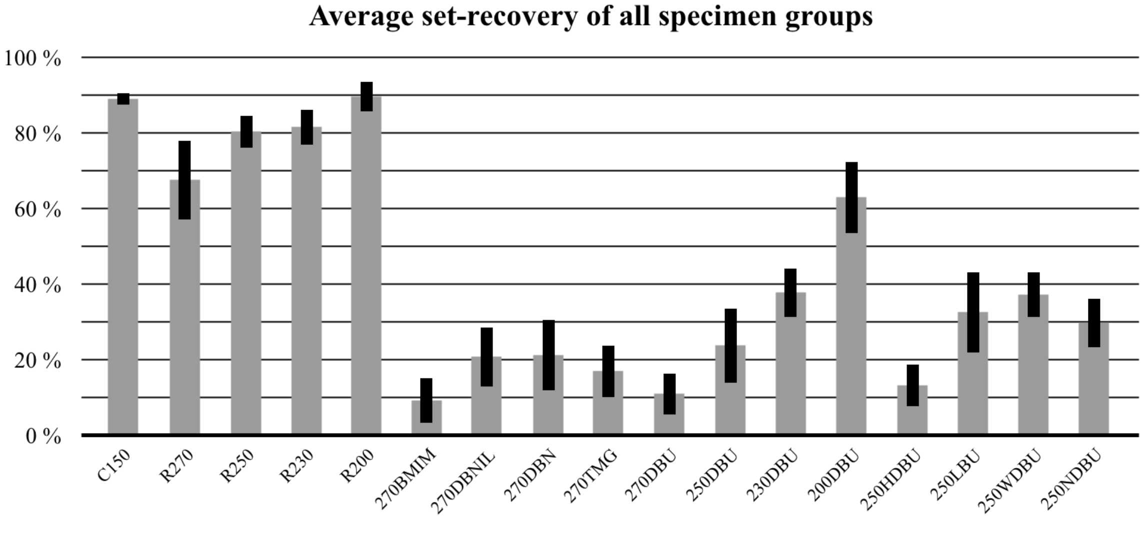

Figure 1: The grey bars show the average set-recovery of all specimen groups, and the error bars show ±1 standard deviation.

In general, the treatment with ILs and organic superbases led to a strong reduction in set-recovery (Figure 1). There was no significant difference in set-recovery between the first and second wet-dry cycles. The grey bars in Figure 1 show the average set-recovery of the specimen groups after two wet-dry cycles, while the error bars show ±1 standard deviation. Most groups that were exposed to a high temperature during the treatment show a high intra-group variation in set-recovery, primarily due to outliers that had a considerably higher set-recovery than the other specimens. Based on the colour changes of the wood surface caused by the high densification temperature, we suspect that an uneven temperature distribution within the heated press platen was responsible for this.

Depending on the pressing time, the set-recovery could be reduced from about 90% (C150 & R200) to as low as 10% for the 270BMIM and 270DBU groups. This reduction in set-recovery can be attributed both to the heat and to the chemical treatment, but the set-recovery of groups R200-270 shows that the effect of heat, i.e. thermal degradation was much less than the effect of the chemical treatment.

A comparison of the 250DBU, 250HDBU and 250LDBU groups, with respectively 20%, 30%, and 10% concentration of DBU in ethanol indicates that an increase in concentration leads to a reduction in set-recovery, but further studies are needed to determine the precise character of this relationship.

The set-recovery of the 250WDBU group (MC = 5%) suggests that moisture is detrimental to the efficacy of the pre-treatment with DBU, as we expected based on published studies of the dissolution of cellulose in ILs (Mäki-Arvela *et al.* 2010). Nevertheless, the decrease in set-recovery was substantial.

The surface of the specimens of almost all the groups was punctured with small holes in order to facilitate penetration of the chemical solutions into the wood. Surprisingly, the set-recovery of the 250NDBU group without holes was only slightly higher than that of the 250DBU group – which was otherwise pre-treated and densified in the same way. Puncturing of the surface is perhaps unnecessary.

Figure 2 shows the relationship between the average set-recovery and the densification temperature. The light curve corresponds to the C150 & R200-270 groups, and the dark curve corresponds to the 270-200DBU groups. It can be seen that the reduction in set-recovery increases with temperature, and in the case of the specimens treated with DBU, the relationship appears to be almost linear. We suggest to investigate even higher temperatures and also lower temperatures for the pre-treated specimens in order to obtain a more complete picture of the relationship between set-recovery and temperature.

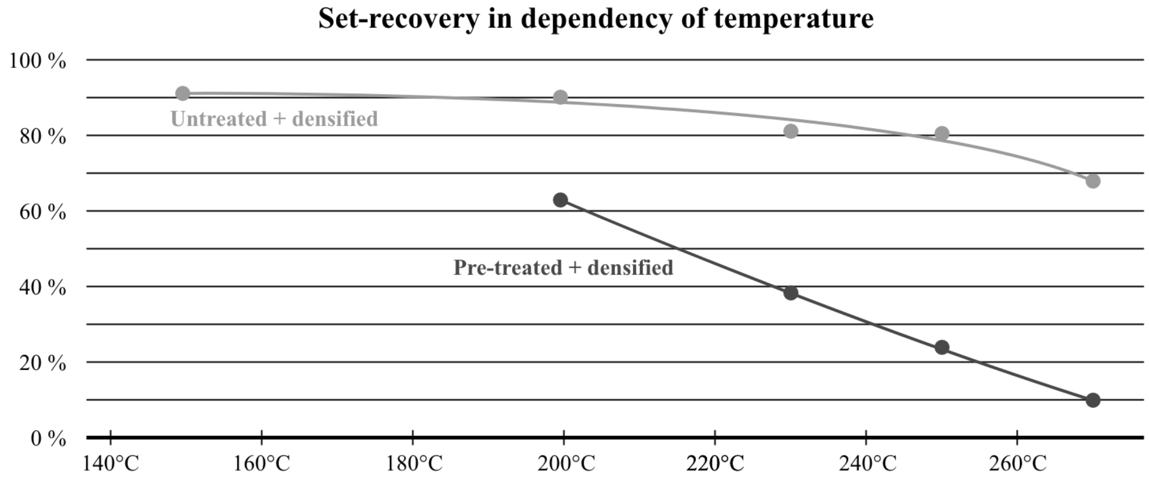

***Figure 2:** Average set-recovery as a function of the densification temperature. The dark curve corresponds to groups C150 and R200-270, while the light curve corresponds to groups 200-270DBU.*

CONCLUSIONS

The results indicate the suitability of ionic liquids (1-Butyl-3-methylimidazolium chloride and 1,5-Diazabicyclo(4.3.0)non-5-enium propionate) and organic superbases (1,5-Diazabicyclo(4.3.0)non-5-ene, 1,8-Diazabicyclo(5.4.0)undec-7-ene and 1,1,3,3-Tetramethylguanidine) as strong plasticisers to reduce the elastic component of deformation of wood under load. The elastic spring-back is completely eliminated, and the set-recovery is reduced to an extent that is dependent on the densification temperature and the concentration of the chemical solution. The superbases have an effect more or less equally as strong as the ionic liquids. At this point, it is not clear why the treatment with superbases has an effect similar to that of the treatment with ionic liquids, and we have therefore planned additional experiments to gain a better understanding of the chemical mechanisms involved in the pre-treatment with ILs and organic superbases.

The process described here can be seen as a precursor to the development of a continuous open system densification process, because a closed system is not necessary and both the chemical treatment and the densification stage have the potential to be performed in a continuous manner. Further studies are however needed to optimize the treatment.

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Potential solutions for gluing acetylated wood in load bearing constructions

Andreas Treu[1], Ronny Bredesen[2] and Ferry Bongers[3]

[1]Norwegian Institute fo Bioeconomy Research, Pb. 115, 1431 Ås, Norway, [email: ant@nibio.no]

[2]Dynea AS, P.O. Box 160, 2001 Lillestrøm, Norway, [email: ronny.bredesen@dynea.com]

[3]Accsys Group, Product Development Manager, P.O. Box 2147, 6802 CC Arnhem, The Netherlands, [email: ferry.bongers@accsysplc.com]

Keywords: Acetylation, gluing, hydroxyl accessibility, Melamine Urea Formaldehyde, Radiata pine, timber bridges

ABSTRACT

Acetylated wood is a durable and dimensional stable product and has high potential for exterior timber structures. Research has shown that acetylated wood can be effectively bonded by various adhesive types. However, one of the most common used adhesives for timber constructions, Melamine Urea Formaldehyde (MUF), shows a bad performance in combination with acetylated wood when tested for resistance to delamination based on cyclic wetting and drying. The less polar acetylated wood surface leads to reduced adhesion due to poorer adhesive wetting of the wood and fewer chemical bonds between the two surfaces.

The use of a primer on the wood surface prior to the application of the glue leads to positive results. In addition, PRF adhesive systems showed high resistance against delamination and can be used for gluing of acetylated wood.

INTRODUCTION

A sustainable future for wood products depends partly on extending the service life of wood. Acetylated wood is a durable and dimensional stable product and has high potential for load-bearing, exterior timber structures. Due to the acetylation process, several wood properties alter which have an impact on the gluing properties of acetylated wood in timber structures for outside applications.

Gluing of acetylated has been investigated using different types of adhesives (Vick *et al.* 1993, Frihart *et al.* 2004, Frihart *et al.* 2017). The reduced wettability and the limited capacity of the acetylated wood to absorb water from the curing bond-line have an impact on the choice of adhesive. Many adhesives contain polar polymers so that their adhesion is diminished in proportion to the presence of the non-polar and hydrophobic acetate groups in acetylated wood (Vick and Rowell 1990). One of the most common used adhesives for timber constructions, Melamine Urea Formaldehyde (MUF), shows a poor performance, when tested for resistance to delamination in combination with acetylated wood. The less polar acetylated wood surface leads to reduced adhesion due to poorer adhesive wetting of the wood and fewer chemical bonds between the two surfaces (Brandon *et al.* 2005, Hunt *et al.* 2007). However, the improved dimensional stability of acetylated wood results in less shrinking and swelling stresses on the cured adhesive bond (Ormstad 2007, Sernek *et al.* 2008).

It was the aim of a Norwegian project (GlAceWood) to investigate the use of MUF-glued acetylated wood for load-bearing constructions for application in service class 3 (Treu *et al.* 2017). The specific objectives were to investigate the factors that influence the gluing of acetylated wood and to overcome the poor gluing performance of MUF-glued acetylated Radiata pine.

EXPERIMENTAL

Wood samples

Radiata pine (*Pinus radiata*) and beech (*Fagus sylvatica*) wood were used for the gluing trials. The wood material was acetylated according to the commercial production process for Accoya at Accsys Technologies.

Six lamella with dimensions of 30 x 150 x 500 mm^3 respectively 22 x 100 x 500 mm^3 were glued together to a bonded member using 15 minutes closed assembly time (CAT) for Melamine Urea Formaldehyde (MUF) and 30 minutes for Phenol Resorcinol Formaldehyde (PRF) adhesive system, starting after the last lamella has been added to the member. The members were assembled by two people in the laboratory. In case of primed and MUF-glued samples, one person was applying the primer and the other person applying the glue. This lead to increasing assembly time from the first to the fifth glue line with a time difference of about 10 minutes. The closed assembly time for primed and MUF-glued samples is therefore 15 minutes for the last glued lamella, while all other lamellas had longer closed assembly time, with a maximum of 25 minutes. The wood members were pressed overnight and acclimatised at standard climate 20°C/65% RH for a minimum of 7 days.

Delamination test and analysis of penetration depth

From the full cross-section of each of the laminated member, four test samples were cut and tested for resistance to delamination according to EN-302-2:2013. One test sample per member with dimensions of 180 x 150 x 50 mm^3 for Radiata pine and 130 x 100 x 50 mm^3 for beech was analysed for penetration depth of adhesive and primer.

The transverse surface of the test sample was either sanded, using a fine sanding paper (P400 paper), or cut into three smaller samples per glue line and prepared by a microtome.

The first method left wood dust in the cell lumina during the sanding process, while the second method opened the cell lumina. See Figure 1 - 5 which shows the glue line, surrounding tracheids and rays for transverse sections of test samples prepared by a sander or by a microtome.

Each glued test sample consisted of 6 lamella and 5 glue lines. Measurements of penetration depths were performed at each glue line. 30 measurements above and 30 measurements below each glue line were performed using the ZEN2 (2011) software-based measuring tools in combination with a Zeiss Axio Zoom V.16 microscope in 20x magnification. The measurement of penetration depth was done mostly along the rays in radial direction.

Adhesive systems

Two adhesive systems were used, Melamine Urea Formaldehyde (MUF) and Phenol Resorcinol Formaldehyde (PRF). The MUF was mixed together with the hardener in a glue mix of 100:100 m/m and spread one-sided with an application amount of 250 g/m^2. The PRF was mixed together with the hardener HRP 155 in a glue mix of 100:20 m/m and spread one-sided with an application amount of 350 g/m^2. The wood surface was primed with a resorcinol-based primer with 80 g/m^2 prior to the application of the MUF adhesive. An overview of the samples is shown in Table 1.

Table 1: Overview of wood samples, treatment and adhesives used in this study (N = total number of glue lines analysed for resistance to delamination)

Wood species	Treatment	surface modification	Adhesive	N
Radiata pine	Acetylated	-	PRF	60
Radiata pine		Primer	MUF	120
Beech		-	PRF	60
Beech		Primer	MUF	120
Radiata pine	Untreated	-	MUF	120
Radiata pine		Primer	MUF	120
Beech		Primer	MUF	120

RESULTS AND DISCUSSION

Comparison of surface preparation

Sanding of the transverse surface led to accumulation of white-coloured wood powder in the cell lumina. The sanded surfaces made the primer more visible. The measurement of the primer-penetration and the PRF penetration could be performed successfully. However, the MUF glue could not be detected using either method.

Using a microtome for cutting the surface area of smaller samples led to open cell lumina and better visibility of glue in the cell lumina. The MUF glue was, however, mixed with the primer and it was often impossible to distinguish between the primer and glue by visual examination only. We chose therefore to use the sanding method for surface preparation and to measure only the penetration depth of the primer and the PRF glue. Other investigations on the analysis of adhesive penetration utilize microscope slide sections (Sernek *et al.* 1999), fluorescence microscopy (Johnson and Kamke 1992, Bastani *et al.* 2015, Bastani *et al.* 2016) or even more sophisticated methods (Hass *et al.* 2009).

Penetration of primer and adhesive

The penetration of the MUF alone could not be measured, since it assumingly was combined with the primer during assembling and has therefore got an orange/yellow colour. The penetration measurement depends on the sample surface preparation method. From the two methods tried, sanding was chosen to be more efficient and practical. The wood sample’s transversal sides were sanded with P400 and the radial penetration of the primer was measured on the transverse section.

The primer penetration was mainly measured in the rays in radial direction and is considered as a maximum penetration. The mean maximum penetration of UF adhesive in beech wood has been reported to be below 0.4 mm (Sernek *et al.* 1999), while PRF in acetylated Radiata pine showed a mean maximum penetration in the rays of 0.75 mm in our study (Table 2). This is comparable to the maximum penetration of a one-component polyurethane (PU) adhesive in Scots pine (Bastani *et al.* 2016).

The primer showed higher penetration depths compared to PRF and even higher penetration in acetylated Radiata pine compared with untreated Radiata pine. The higher penetration of the primer could also mean a higher penetration of the MUF glue, if primer and glue is mixed during assembling of the wood samples. An excessive penetration may result in a starved glue line (Marra 1992), which has been observed in the case of MUF bonded acetylated wood. However, the application of the primer lead to an increase in the resistance to delamination

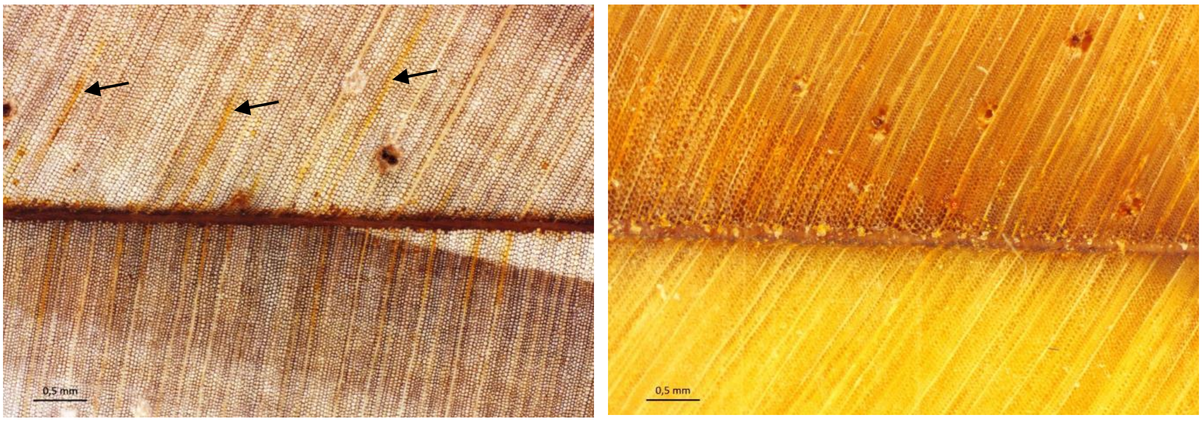

Figure 1 (left) and Figure 2 (right): Glue line region of untreated Radiata pine prepared by sanding (left) or microtome (right); primer (orange coloured, mainly in the rays, see arrows) and MUF adhesive was used in both samples

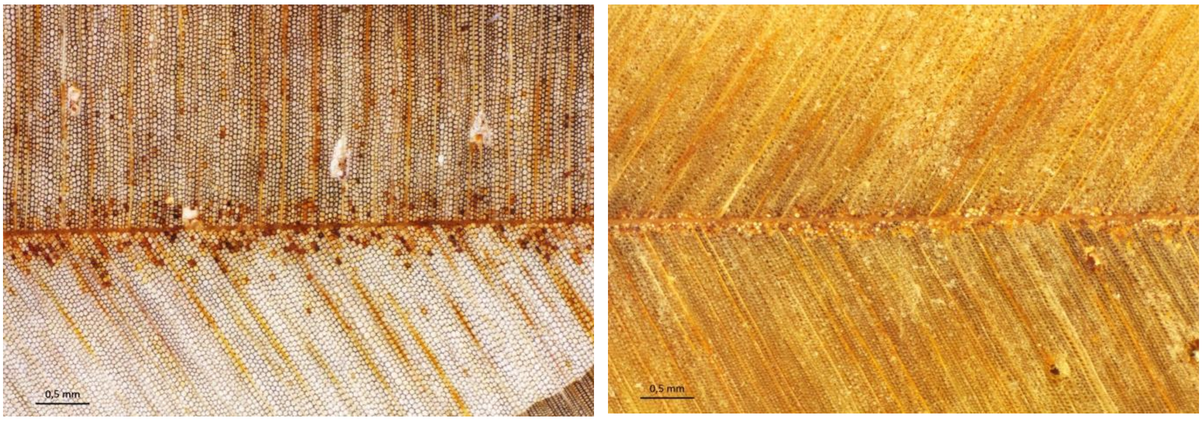

Figure 3 (left) and Figure 4 (right): Glue line region of acetylated Radiata pine prepared by sanding (left) or microtome (right); primer (orange coloured, mainly in the rays and cell lumina) and MUF adhesive was used in both samples

Figure 5: Glue line region of acetylated Radiata pine prepared by sanding; a PRF adhesive system was used in this samples

Resistance to delamination of MUF-glued wood

It is understood from the literature that the preferential wood adhesive system, in our case MUF, cannot be used without modifying the wood surface or the adhesive system itself (Vick and Rowell 1990, Bongers *et al.* 2016, Treu *et al.* 2017). Changing the gluing process alone will not lead to a successful outcome. Earlier trials on acetylated Radiata pine and beech using MUF support this by showing 90-100% delamination in most of the cases.

In contrast, the delamination of acetylated Radiata pine in this study was significantly reduced by using a resorcinol-based primer in combination with MUF, see Figure 6 and Table 2. The resorcinol-based primer is assumingly improving the wettability and the surface energy. Using resorcinol-formaldehyde adhesive on acetylated yellow poplar showed durable bonds independent on the degree of acetylation (Frihart *et al.* 2017). The role of the resorcinol-based primer in our study remains unclear.

The average delamination of acetylated beech could only slightly be reduced by applying a primer to the wood surface. Delamination results show a higher variation for primed and acetylated beech compared with primed and acetylated Radiata pine.

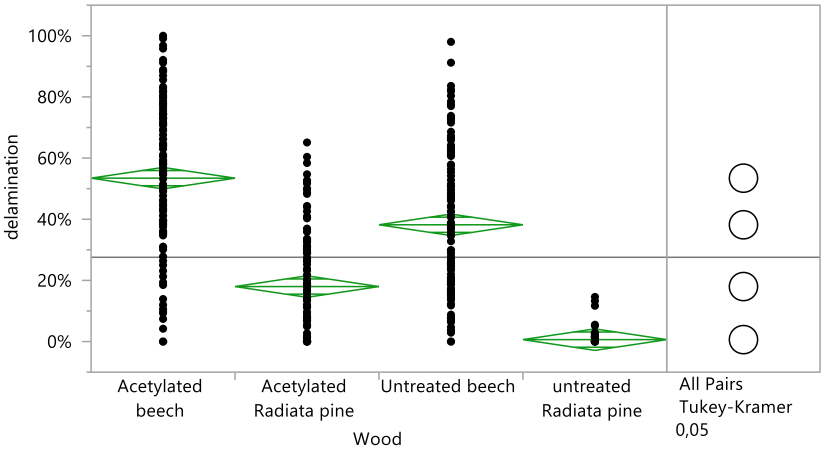

Figure 6: Overview over delamination of MUF-glued and resorcinol-primed samples per treatment and wood species. The data include the separate measurements of 5 glue lines and 4 delamination samples. The mean values are significantly different for all treatment/wood species factors.

Glue lines of MUF-glued wood

We found significant differences in delamination depending on the glue line for both acetylated Radiata pine and beech (see Figure 7 and 8), which could explain the high variation in delamination. While acetylated Radiata pine showed a tendency of decreasing delamination with decreasing closed assembly time (from GL1 to GL5) no trend could be seen for the delamination depending on glue line or assembly time for acetylated beech. The unintended differences in assembly time per glue line is caused by limited working speed in laboratory conditions and shows the sensitivity and the importance of an optimized process.

Glue lines 4 and 5 of acetylated and primed Radiata pine wood samples showed in average less than 20% delamination. We hypothesize that several process-related approaches could further reduce the delamination, such as increasing the amount of adhesive per bond line or using different concentrations of adhesive and hardener in the glue mix.

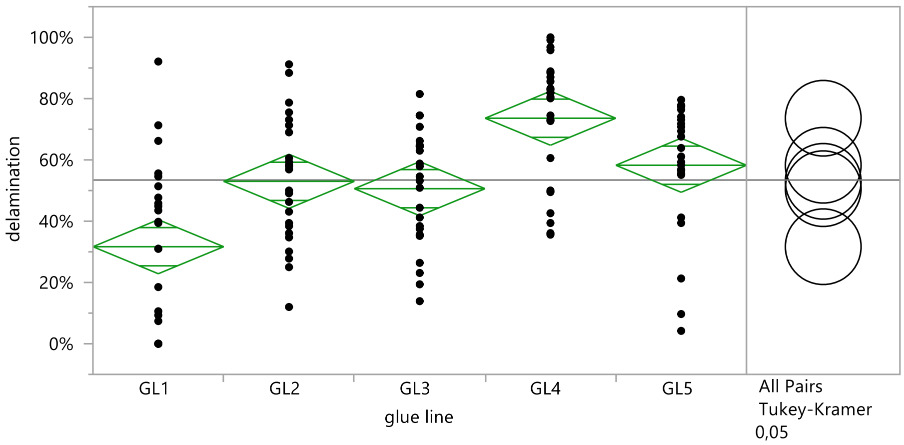

Figure 7: Delamination [%] of MUF-glued and resorcinol-primed acetylated beech, divided by glue line (GL1-GL5)

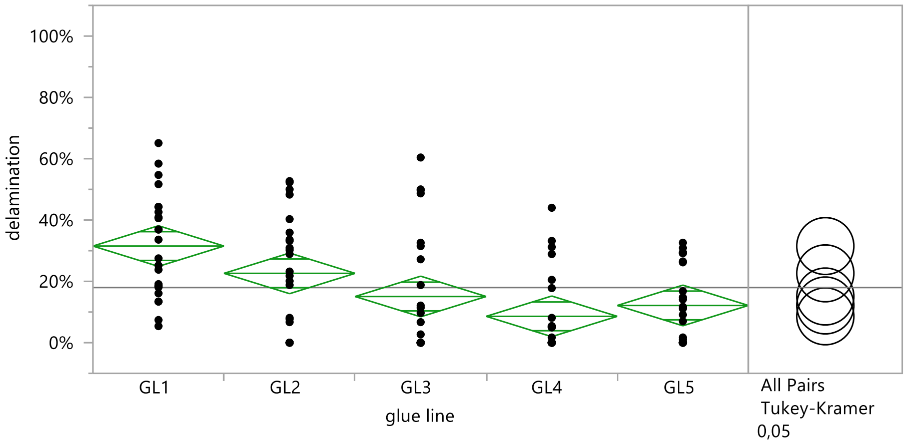

Figure 8: Delamination [%] of MUF-glued and resorcinol-primed acetylated Radiata pine, divided by glue line (GL1-GL5)

Table 2: Delamination and penetration of primer/adhesive

Wood species	**treatment**	**surface modification**	**Adhesive**	**delamination [%]**	**STDV**	**Penetration Depth [mm]**	**STDV**
Radiata pine	acetylated	-	MUF	90-100*	-	- **	- **
Beech		-	MUF	90-100*	-	- **	- **
Radiata pine		-	PRF	0	0	0,752	0,18
Radiata pine		Primer	MUF	17,9	18	1,728	0,42
Beech		-	PRF	0,22	1	- **	- **
Beech		Primer	MUF	53,4	25	- **	- **
Radiata pine	untreated	-	MUF	0,2	1	-	-
Radiata pine		Primer	MUF	0,6	2	1,072	0,31
Beech		Primer	MUF	38,2	24		

**The results were obtained in earlier tests*
***The penetration depth was not measured*

Delamination of PRF-glued wood

The PRF adhesive system showed good performance in the delamination tests. PRF is the preferable system according to the delamination results. A PRF system has been successfully used for two acetylated timber bridge constructions “Sneek” in the Netherlands (Jorissen and Luning 2010). However, the PRF systems have a higher price compared to MUF systems and cannot be easily applied with the existing application equipment commonly used to apply MUF. MUF systems are used today for gluing nearly 80% of all glulam in Europe and most producers have not space for additional storage and application equipment or prefer to handle only one adhesive system.

CONCLUSIONS

Using a resorcinol-based primer could significantly reduce the delamination of acetylated Radiata pine. However, a large variation in delamination is observed within the glued samples of acetylated Radiata pine. The effect the primer has on gluing acetylated beech is smaller compared with Radiata pine.

The observed differences in delamination per glue line and the trend of having higher delamination in glue line 1 and lower delamination in glue line 5 in acetylated Radiata pine could be explained by the time factor during assembling. However, further investigation needs to include as well the role of annual ring angle and earlywood content at the glue line.

The PRF adhesive system showed high resistance to delamination and can be used for gluing of acetylated wood.

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Combustion behaviour of wood chemically modified with DMDHEU-, PF-, and MF- resins

Zhijun Zhang[1], Zefang Xiao[1], Holger Militz[2], Carsten Mai[2], Yanjun Xie[1]

[1]Key Laboratory of Bio-based Material Science and Technology (Ministry of Education), Northeast Forestry University, 150040, 26 Hexing Road, Harbin, P. R. China [email: zzj_1003@163.com; zxiao@nefu.edu.cn; yxie@nefu.edu.cn]

[2]Wood Biology and Wood Products, Georg-August-University of Goettingen, Buesgenweg 4, 37077, Goettingen, Germany [email: hmilitz@gwdg.de; cmai@gwdg.de]

Keywords: chemical modification; combustion; heat release; scanning electron microscopy; smoke suppression; wood.

ABSTRACT

Modification of wood with 1,3-dimethylol-4,5-dihydroxyethyleneurea (DMDHEU), phenol formaldehyde (PF) resin, and melamine formaldehyde (MF) resin is known to be efficient strategy to improve wood's dimensional stability, mechanical strength, and durability. The combustion behaviour of these modified woods is also important when they are used in the public domain. This study systematically examined the effects of these types of modifications on the combustion behaviour of wood treated to weight percent gains ranging from 10 to 55%. Cone calorimetry showed that the DMDHEU-treated wood released comparable heat and smoke to the untreated wood (Figure 1). The PF treated wood was more difficult to ignite and yielded more char than the untreated control. Treatment with PF did not substantially change the heat release of wood but led to a considerably increase in CO and smoke production due to incomplete combustion (Figure 5). Treatment of the wood with MF caused greater heat release due to complete combustion; however, smoke production was significantly suppressed. These findings demonstrate that DMDHEU treatment did not cause any substantial effect on the combustion performance of the wood. MF treatment can reduce the fire risk in Scots pine wood; however, the high CO concentrations and dense smoke produced by burning the PF-treated wood are seen as potential problem.

INTRODUCTION

Chemical modification of wood by impregnation with aqueous solutions is known as an efficient strategy to improve the dimensional stability and durability of wood, especially in fast-growing plantation species (Militz 1993, Stamm and Seborg 1936, Xie *et al.* 2014). Commonly used chemicals for these techniques include N-methylol resins, acetic anhydride, furfuryl alcohol, and formaldehyde-based resins such as melamine formaldehyde and phenol formaldehyde (Xie *et al.* 2013, Klüppel and Mai 2013). These modified wood exhibits potential application in the construction of public venues, such as stadiums, subway stations, airports, and hotels. Apparently, fire safety is an important concern in these public places. However, few studies have examined the fire properties of chemically modified wood (Mohebby *et al.* 2007, Pries and Mai 2013). This reported study was devised to reverse this situation by systematically surveying the effects of modification with DMDHEU, PF and MF on the pyrolysis and flame properties of wood in the laboratory, based on testing using thermogravimetry (TG), cone calorimetry (CONE).

EXPERIMENTAL

Wood and chemicals

Parallel-grain oak wood (*Quercus mongolica* L.) and Scots pine (*Pinus sylvestris* L.) sapwood deforested in Lower Saxony of Germany were cut into panels measuring 100 × 100 × 10 mm^3 (longitudinally × radially × tangentially) and used for cone calorimeter testing. 1,3-Dimethylol-4,5-dihydroxyethyleneurea (DMDHEU), phenol-formaldehyde (PF) and melamine-formaldehyde (MF) resins used in this study were commercially-available, ready-to-use aqueous solutions. DMDHEU were received from BASF (China) Co. Ltd. (Shanghai, China); the active content of 45%. PF resin was provided by Cytec Surface Specialties GmbH & Co. KG (Wiesbaden, Germany); the solid content was approx. 60% and the average molecular weight was approx. 400. The MF resin was provided by Ineos Melamines GmbH (Madurit MW840/75WA, Frankfurt, Germany); the solid content was approx. 75% and the average molecular weight was approx. 840. $MgCl_2$ and triethanol amine purchased from Alfa Aesar (Tianjin, China) served as catalysts. NaOH (technical grade) was used to adjust the pH value of the treating solutions.

Wood modification

Wood specimens were oven dried at 103 °C for 24h. The specimens were fully impregnated, under vacuum (100 mbar, 0.5h) followed with pressurizing in compressed air (10 bar, 0.5h), in the aqueous solutions detailed below:

(1) 10, 20, and 30% PF resin, respectively; the solution pH value was adjusted to 10.0 by adding NaOH. The treated wood specimens are abbreviated in the context as $W_{10\%PF}$, $W_{20\%PF}$, and $W_{30\%PF}$, respectively.

(2) 10, 20, and 30% MF resin, respectively; triethanol amine (1% of solid content of MF resin) was used as a catalyst; the solution pH value was adjusted to 10.0 by adding NaOH. The treated wood specimens are abbreviated in the context as $W_{10\%MF}$, $W_{20\%MF}$, and $W_{30\%MF}$, respectively.

(3) 10% DMDHEU or 10% DMDHEU plus 1.5% $MgCl_2.6\ H_2O$, respectively.

The impregnated wood specimens were dried in air to a moisture content of approx. 25% and then oven dried at 40°C for 24h, followed by drying at 120 °C for 24h. The untreated wood (abbreviated as W_{CTRL}) served as control. Ten replicates were used for each treatment. The average weight percent gains (WPG) of the treated samples were calculated by subtraction method. The WPGs of PF and MF treated wood were controlled ranging from 10 to 55% by regulating the concentration of monomers. The DMDHEU treated samples attained an average weight percent gain (WPG) of 5.5 and 6.3%, respectively.

Thermogravimetric analysis

The wood particles passing an 80-mesh sieve and retaining in the 100-mesh sieve were collected. About 5 mg sample was placed into the thermal analyzer (TGA 209 F3, Netzsch Co., Germany); purge gas: N_2 60 ml min^{-1}, heating: from r.t. to 800 °C (10 °C min^{-1}). Measurements were repeated in triplicate for each treatment. The curves of residual mass (RM) and its derivative (DTG) were recorded through the tests.

Cone calorimetric test

The tests were performed in the instrument (Fire Testing Technology Ltd, East Grinstead, UK) according to the standard ISO 5660-1, 2002. The sides and rear surface of the wood sample were wrapped with aluminum foil only leaving the upper surface exposed to the fire; heat flux: 50 $kW.m^2$. The untreated and treated wood specimens were oven dried before testing to eliminate the effects of moisture. The data on heat release, smoke production, and amount of charcoal were recorded. The tests were repeated three times for each treatment.

RESULTS AND DISCUSSION

DMDHEU-treated wood

Time to ignition (TTI) and fire performance index (FPI): At a heat flux of 50 kW.m^2, untreated wood (W) was set alight after 19s (Table 1). Treated wood exhibits a shorter time to ignition (TTI). W_{DMDHEU} has the shortest TTI and $W_{DMDHEU+MgCl2}$ has a slightly longer ignition time. The fire performance index (FPI) – the ratio of TTI and the maxima of the initial peak of heat release rate – characterizes well the fire risk of a material (Marney *et al.* 2008). W_{DMDHEU} has the lowest FPI value (Table 1), while the FPI of $W_{DMDHEU+MgCl2}$ is the highest.

Table 1. Results of fire tests from treated and untreated oak specimens.

			Char yield (%)		**Reaction to fire**		
Treatment	**TTI [s]**	**FPI [m^2 s kW^{-1}]**	**TG**	**CONE**	**CHF [kW m^{-2}]**	**Fs [mm]**	**SP [%×min]**
Untreated	19 (1)	0.049 (0.008)	17.6 (0.3)	17.7 (0.8)	3.4	<150	224
DMDHEU	16 (1)	0.032 (0.012)	15.7 (0.7)	18.2 (1.2)	-	-	-
DMDHEU +$MgCl_2$	17 (2)	0.042 (0.011)	22.4 (0.5)	19.2 (0.9)	3.2	<150	196

Time to ignition (TTI), fire performance index (FPI), and combustion residues obtained after TG and CONE test, critical heat flux (CHF), vertical flame spread within 20 s (Fs) and smoke production. (The values in the parentheses show the standard deviation of three replicates).

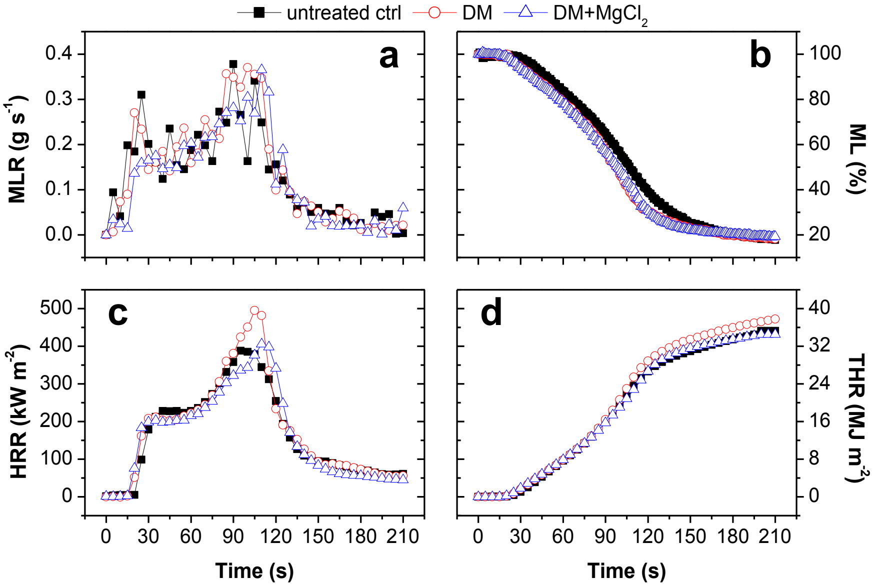

Figure1: Results of combustion tests: mass loss rate (MLR, a), mass loss (ML, b), heat release rate (HRR, c), and total heat release (THR, d) of untreated and treated wood.

Mass loss and heat release: The mass loss rates (MLR) of untreated and treated woods are scattering because of the pulsating combustion (Figure 1a). Two peaks at approx. 30 and 100 s are visible, which correspond to the flaming and glowing combustion of wood, respectively. The mass retention of W was greater than that of W_{DMDHEU} with or without $MgCl_2$ (Figure 1b). All specimens exhibit similar ML at the end of the process. DMDHEU treatments do not facilitate char formation. Therefore, around 32% of the carbon in the treated wood is volatilized. The heat release rate (HRR) of wood rapidly increases after the initial 30s (flaming stage) and the maximum peak occurs at 100 s (glowing period). Subsequently, the rate decreases and levels off after 150s (Figure 1c). The peaks located at ca. 30 and 100s are the exothermic reaction during the combustion of flammable pyrolysates. Treatments with DMDHEU with or without $MgCl_2$ do not substantially influence the heat release rate of the wood in the initial 90s, over which W_{DMDHEU} show a higher heat release rate than the untreated control (W). The maximum HRR peak of W_{DMDHEU} and $W_{DMDHEU+MgCl2}$ have a similar intensity to that of W but the time range is broader. W_{DMDHEU} has the highest total heat release but the data of all samples are very similar (Figure 1d).

Smoke products: The smoke production rate (SPR) of the untreated wood increases with the combustion time and rapidly reaches the first peak located at ca. 30s (Figure 2a). The SPR of woods treated with DMDHEU with and without $MgCl_2$ are very similar between 30-90s, but apparently lower than that of W. This is probably due to higher heat produced by burning of DMDHEU, which promotes the complete combustion of wood polymers. The total smoke production of the untreated wood is higher than that of the treated wood (Figure 2b).

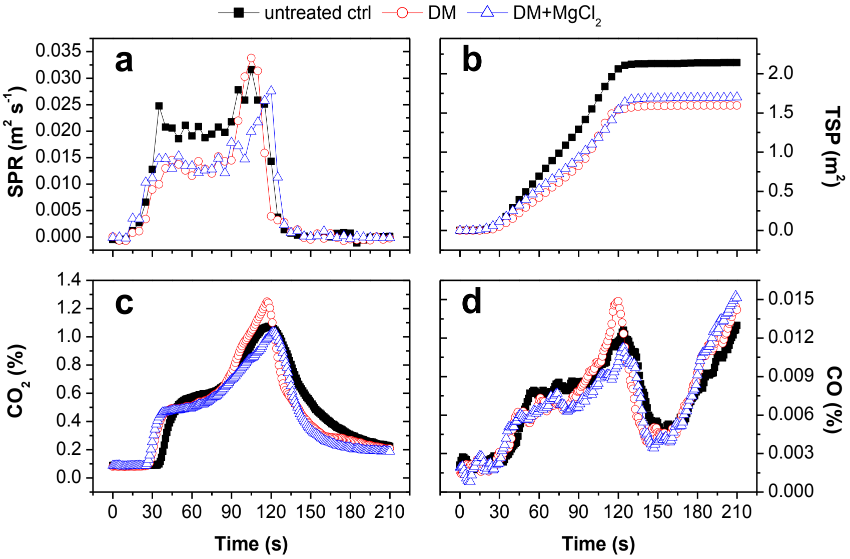

Figure 2. Results of combustion tests: mass loss rate (MLR, a), mass loss (ML, b), heat release rate (HRR, c), and total heat release (THR, d) of untreated and treated wood.

Yield of carbon oxide: A rapid CO_2 increment after 37 s combustion (Figure 3c) is typical. Between 35 to 75s (flame burning), the CO_2 development is slowed down. The treated woods release CO_2 earlier than W. At around 120s, $W_{DMDHEU+MgCl2}$ exhibits comparable CO_2 development to that of W, and the CO_2 concentration of W_{DMDHEU} was even higher than that of W at around 120s, indicating a greater flashover. The CO is mainly generated in the period of flaming and glowing combustion (between 40-150s) and the data are scattering (Figure 3d). W_{DMDHEU} shows the highest intensity at around 120s while $W_{DMDHEU+MgCl2}$ reveals a lower CO development compared of W.

PF and MF treated wood

Time to ignition (TTI) and fire performance index (FPI): The W_{CTRL} and $W_{10\%PF}$ ignited after 19s, but treatment with increased concentrations of PF caused longer TTI (Table 2). All MF treated wood exhibited a comparable TTI that was longer than the W_{CTRL}. The FPI values for the PF and MF treated woods increased by 41% (Table 2). This suggests a reduction in fire risk for these treated woods.

Table 2. Temperature at starting decomposition (Ts) and at inflection point (Tf) at two stages of wood thermal decomposition determined by TG analysis, and time to ignition (TTI), fire performance index (FPI), and residual mass (RM) determined by CONE calorimetric test.

	TG				**CONE**		
Treatment	**1st stage**		**2nd stage**				
	T_s (°C)	**T_f (°C)**	**T_s (°C)**	**T_f (°C)**	**TTI (s)**	**FPI (m^2 s kW^{-1})**	**RM (%)**
Untreated	294.9 (2.21)	314.2 (0.64)	420.1 (7.32)	433.1 (0.35)	19 (2)	0.073 (0.008)	18.3 (0.7)
10% PF	258.8 (0.28)	294.2 (2.75)	396.4 (0.21)	412.9 (0.07)	19 (1)	0.079 (0.004)	26.8 (0.5)
20% PF	*ND*				26 (3)	0.102 (0.015)	31.0 (0.2)
30% PF	278.5 (0.78)	308.2 (0.28)	415.5 (0.07)	431.2 (1.77)	30 (2)	0.101 (0.009)	33.3 (0.8)
10% MF	275.5 (0.42)	309.9 (0.57)	434.6 (3.18)	462.6 (1.06)	26 (1)	0.103 (0.006)	25.1 (1.1)
20% MF	*ND*				26 (2)	0.103 (0.007)	26.0 (0.3)
30% MF	263.4 (1.56)	301.6 (2.19)	435.2 (8.63)	472.8 (6.34)	29 (3)	0.103 (0.010)	27.9 (0.2)

Note: ND shows non-determined. The values in the parentheses show the standard deviation of three replicates.

Residual mass: Compared with the W_{CTRL}, the wood treated with PF exhibited a residual mass increase of up to 33% as the PF concentration in the treatment solution was increased (Table 2). The residual mass of MF-treated wood was lower than that of the PF-treated wood (Table 2).

Heat release: The untreated and treated woods exhibited two HRR peaks during the combustion process (Figure 3). The first HRR peak (HRR_I) appeared during the initial flaming period. The second HRR peak (HRR_{II}) with a stronger intensity was mainly attributed to massively cracking of the burning wood during the main flaming period. Treatment with various concentrations of PF did not change the intensity of HRR_I (Figure 3a). Compared with the W_{CTRL}, treatment with 10% PF caused a narrower and stronger HRR_{II} that appeared earlier. The HRR_{II} of the wood became broader, had lower intensity, and appeared later as the concentration of PF in the treatment solution was increased. The total heat release (THR) of the PF-treated wood was slightly more than the untreated control at the end of combustion process (Figure 3c).

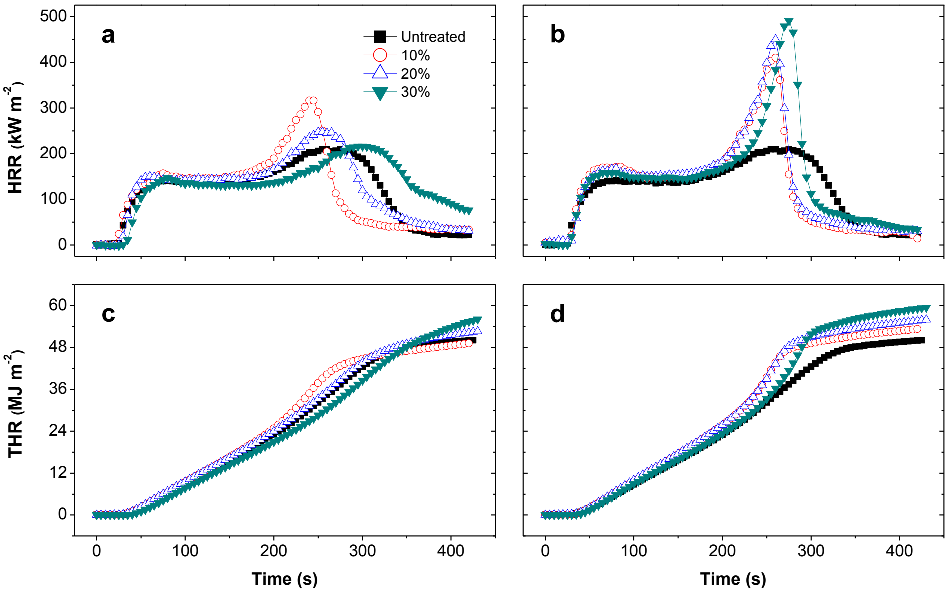

Figure3. Changes heat release rate (HRR, a&b) and total heat release (THR, c&d) of wood untreated and treated with various concentrations of PF (a, c) and MF (b, d) during cone calorimetric test.

Similar to the PF treatment, MF treatments did not substantially change the intensity of $\mathrm{HRR_I}$; however, the intensity of $\mathrm{HRR_{II}}$ was considerably strengthened (Figure 3b). Consequently, the THR of MF-treated wood was higher than that of the $\mathrm{W_{CTRL}}$ during the main flaming period (Figure 3d). It was attributed to partial methylation and methylolation of the MF resin, which produced flammable hydrocarbon compound in the wood (Pittman *et al.* 1994).

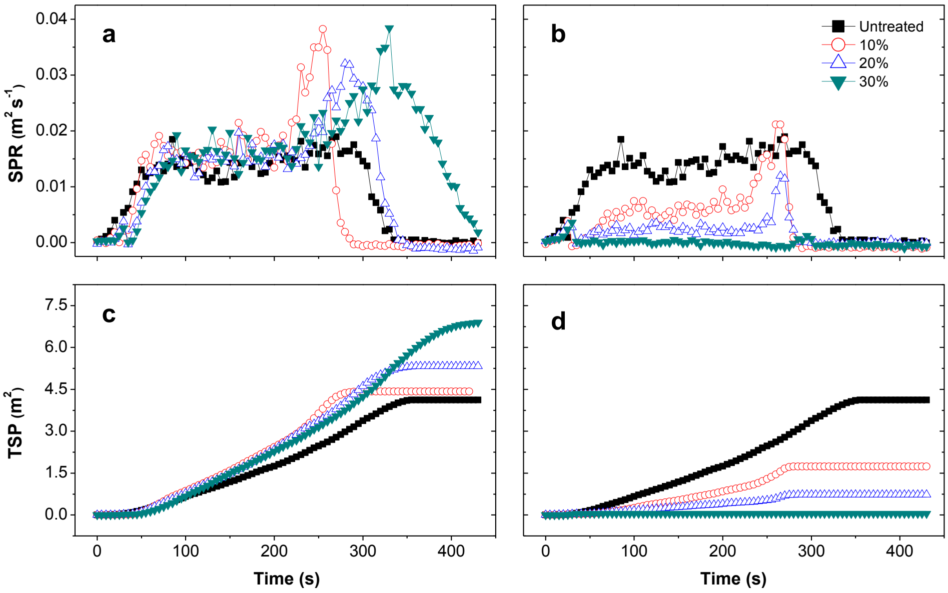

Figure 4. Smoke production rate (SPR, a&b) and total smoke production (TSP, c&d) of wood untreated and treated with various concentrations of PF (a, c) and MF (b, d) during cone calorim. test.

Smoke production: The SPR of $\mathrm{W_{CTRL}}$ increased rapidly in the initial 50s of combustion and then remained stable (Figure 4a). Compared with the SPR curve of the $\mathrm{W_{CTRL}}$, an abrupt SPR peak appeared during the main flaming period of the PF-treated wood. This peak was postponed and became broader with increased PF concentration. As a result, the TSP of PF treated wood was denser than the $\mathrm{W_{CTRL}}$ (Figure 4c). Compared to the $\mathrm{W_{CTRL}}$, the SPR of MF-treated wood decreased considerably with increase in the MF concentration (Figure 4b). As a result, the TSP was accordingly reduced (Figure 4d). The TSP was suppressed almost completely for the wood treated with 30% MF. This implies that light gases such as CO_2, CO, and N_2, rather than the smoke (high-molecular-weight fragments) were formed during combustion (Girods *et al.* 2008; Wang *et al.* 2012). The low TSP may result in a decrease in the smoke hazard during fires, thereby making the MF-treated wood suitable for use in public places.

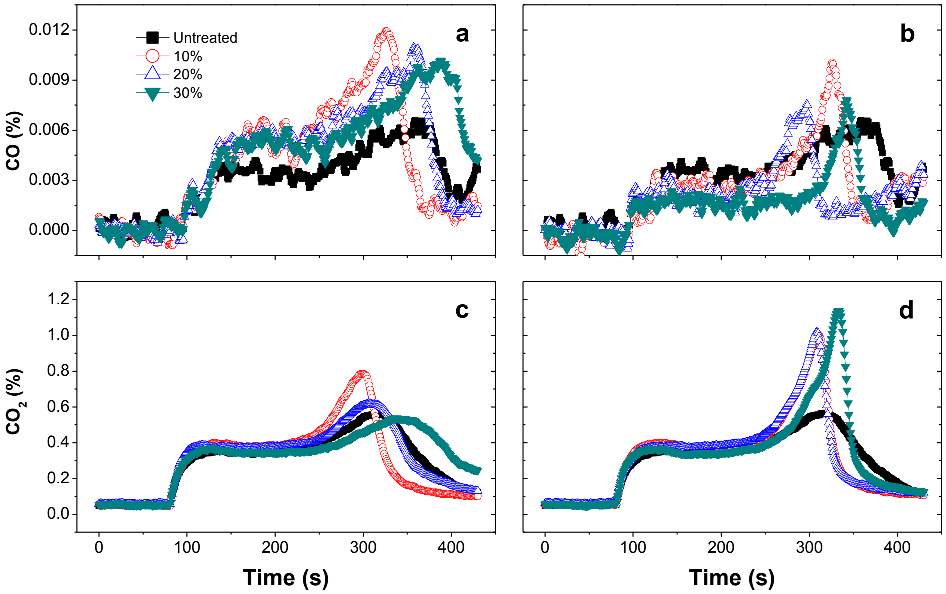

Figure 5 Changes in concentration of CO_2 (a, b) and CO (c, d) of wood untreated and treated with various concentrations of PF (a, c) and MF (b, d) during cone calorimetric test.

Yield of carbon oxide: Compared with the W_{CTRL}, the PF-treated wood produced higher amounts of CO during combustion, especially during the main flaming stage (Figure 5a). Treatment with PF did not substantially influence the amount of CO_2 produced during combustion of the wood (Figure 5c). In contrast to the PF-treated wood, the MF-treated wood yielded considerably lower amounts of CO than the W_{CTRL} during combustion (Figure 5b). However, the amount of CO_2 produced by the MF-treated wood apparently increased during the flaming combustion period (Figure 5d), which is consistent with a higher HRR as shown in Figure 6b. These results further suggest that MF promoted complete combustion of the wood.

CONCLUSIONS

DMDHEU treatment promotes the combustion of oak wood due to flammability of the condensed DMDHEU polymer. Combined treatment with DMDHEU and MgCl2 did not substantially influence the combustion behaviour of the resulting wood but $MgCl_2$ in traces acts as a flame retardant and offsets the flammability of DMDHEU. Modification of wood with PF and MF retarded the pyrolysis process of the wood by inflammation retardation and charring promotion. Incorporation of aromatic PF into the wood (cell wall bulking) caused an increase in smoke and CO production during combustion due to incomplete combustion. Compared to the untreated wood, wood modified with MF exhibited significant smoke suppression and CO yields. Generally speaking, MF-treated wood had a lower fire risk than the untreated and PF-treated wood when used in the public places. DMDHEU-modified wood is not suitable for utilization in places where the materials must be fire-retardant.

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SESSION FOUR B

Properties Thermal Modification

Potential to limit variation in durability of thermally modified timber

Joris Van Acker[1] and Jan Van den Bulcke[2]

[1] Ghent University (UGent), Laboratory of Wood Technology (Woodlab), Coupure links 653, BE-9000, Ghent
[email: joris.vanacker@ugent.be]
[2] Ghent University (UGent), Laboratory of Wood Technology (Woodlab), Coupure links 653, BE-9000, Ghent
[email: jan.vandenbulcke@ugent.be]

Keywords: durability, fungal testing, thermal modification, variability

ABSTRACT

Recently several companies have shown interest in and started thermal modification of lightweight tropical hardwoods. Such treatments mainly aims at reducing the overall susceptibility to fungal attack, but should also reduce the variability related to biological durability of the raw material. For this paper treated wood from four companies using different modification schedules was used. The wood at hand was indicated as TMT Fraké and is based on the tropical wood species with the ATIBT name limba. Comparing from each company a commercial sample was merely intended to provide insight in variability differences related to biological durability. Both a Basisdiomycetes test and a soft rot test were used to assess this variability. Although low mass losses were recorded for Basidiomycetes testing with *Trametes versicolor*, ranking according to median mass losses and variability were similar to the results obtained with the soft rot test. This has potential impact on the probability that some individual planks or stakes produced by one of the four companies might lead to earlier failure. The current approach in standardisation of fungal test in CEN TC38 might allow to verify this better than in the past. The fact that the material from the four companies mainly differ in variability underlines the potential to improve on this parameter by optimizing the process parameters.

INTRODUCTION

The variation in natural durability of wood species is of concern related to suitability for applications with a risk of fungal decay. Enhancing different properties of wood by thermal modification might allow not only to increase durability and moisture resistance but could also impact the variability of the treated material.

Thermal modification of wood has evolved over the last decades from laboratory-based research to commercially viable industrial processes. Thermal modification is invariably performed within a temperature range of 180°C to 260°C, with temperatures lower than 140°C resulting in only slight changes in material properties and higher temperatures mostly resulting in unacceptable degradation of the substrate (Hill 2006). Thermal modification or heat treatment intends to improve wood properties. Although changes in physical and mechanical properties are important (Bekhta and Niemz 2003), the increased biological durability is key for new industrial developments (Kamden *et al*. 2002, Tjeerdsma *et al.* 2002). A wide range of industrial productions of thermally modified timber has evolved (Militz 2002). Welzbacher and Rapp (2002) showed that protection against decay of wood that had been thermally modified by one of the four European commercial processes at that time (Plato, ThermoWood, Retified wood or oil heat-treated wood) decreased in the order *Coniophora puteana* > *Coriolus (Trametes) versicolor* > *Oligoporus (Poria) placenta*. Although there was an improvement in biological durability, this was not as good as that achieved previously with laboratory heat-treated wood, showing that performance improvements were possible by producing a more homogeneous product, hence the need for better process control.

When discussing biological durability it is useful to work on improved statistical approach of biological durability of wood related to both outdoor uses in and out of ground contact situations (Van Acker *et al.* 2010a). Starting with Weibull (1951) distribution functions of mass loss data obtained from worst case laboratory Basidiomycetes testing some parameters can be proposed which should be a better start for engineers to come to a comprehensive approach on variability and a probabilistic methodology for service life prediction. The methodology to determine the natural durability of a wood species or the enhanced durability of modified wood is focussing primarily on fungal attack by Basidiomycetes. However when dealing with applications in ground contact also specific soft rot testing should be addressed.

According to EN 335 and ISO 21887 wood in use faces different possible decay mechanisms depending on the conditions of use and the relevant functional organisms related. ISO 21887 defines five use classes that represent different service situations to which wood and wood-based products can be exposed all over the world. Main concern is for the outdoor end uses. Use class 4 (UC4) is defined as the condition of continuous soil or freshwater contact while UC3 is for outdoor use without ground contact. Since the main difference is that soft rot fungi are not able to destroy wood under UC3 conditions there is clearly a difference in assessing performance, natural or conferred durability of wood and wood products.

Up to now both laboratory fungal testing to assess efficacy (e.g. EN 113 and ENV 807) and testing natural durability (CEN/TS 15083-1&2) have only to a limited extent been able to use the results in a probabilistic way. The natural durability testing methodology as implemented now (CEN/TS 15083-1) only uses the median mass loss values of the Basidiomycetes fungus showing the highest mass loss figures to determine a durability class. Durability classes as defined in EN 350 are intended as indicators for service life under specific conditions (focus on outdoor use in ground contact). Clearly, the objective to translate such durability classes for end use out of ground contact (e.g. UC3) introduces several changes in coming to a time to failure assessment. Mainly the fact that besides insects the main wood destroying organisms are Basidiomycetes fungi and the fact that optimal conditions of wetness are mostly not present are two elements that need to be addressed when estimating how long a wood product will last under UC3 conditions.

MATERIALS AND METHODS

Four commercial sets of similar material were assessed both on their compliance with expected durability class and the distribution of fungal resistance of individual planks. All four sets were obtained from the commercial sector and refer to four different treatment processing plants. The thermally modified material is by all producers referred to as TMT Fraké and is based on the tropical wood species with the ATIBT name limba (*Terminalia superba* Engl. et Diels.) originating from West Africa and ranging from Sierra Leone to Angola.

The four sets of material have been used to assess different properties with a focus on variability in biological durability. Although resistance against Basidiomycetes is considered the dominant criterion for exterior out of ground contact applications, also known as use class 3 according to EN 335 (2013), the discussion in this paper is also related to performance in testing with soil-inhabiting micro-organisms known as soft-rotting micro-fungi. The fungal tests performed are described in the standards CEN/TS 15083-1 (2005) for testing with Basidiomycetes and CEN/TS 15083-2 (2005) for soft rot testing. For all tests over 100 replicates were used.

The resistance against Basidiomycetes was tested according to CEN/TS 15083-1 (2005) including leaching. After sterilization two specimens of the same wood species were placed on fungal mycelium in a Kolle flask. Here only results with the test fungus *Trametes versicolor* are presented. Direct contact between wood and overgrown 4 % malt extract agar was avoided by means of stainless steel spacers. The incubation time was 16 weeks. Beech (*Fagus sylvatica* Linneaus) specimens were included as virulence specimens and showed 25.5 % mass loss. After incubation the test specimens were oven-dried and weighed. The percentage mass loss was calculated as defined in CEN/TS 15083-1 (2005), however using ovendry mass at the start as is included by CEN TC38 WG23 for the standard under development EN 113 part 2 intended to replace CEN/TS 15083-1. Durability classes DC1 (or D1) up to DC5 (or D5) are based on median mass losses classified using limit values of 5, 10, 15 and 30 %.

Assessment of the durability against soft rotting micro-fungi was based on CEN/TS 15083-2 (2005). Before exposure, the specimens (oven-dry weight recorded) were impregnated with demineralised water in order to create the ideal moisture condition for fungal attack. Then the specimens were planted vertically into test containers filled with wetted potting soil with 1/5 of their length protruding the soil surface. Beech was used as reference wood species. The test ended after 16 weeks when mass loss of just over 20% of the beech specimens (median mass loss = 20.1%) was reached. At the end of the incubation period the test specimens were oven-dried and weighed. The percentage mass loss after CEN/TS 15083-2 (2005) was calculated. To determine durability classes the x-value was calculated as the ratio between median mass loss of test specimens and median mass loss of the references. Limit values for the durability classes D1 up to D5 are 0.10, 0.20, 0.45 and 0.80.

In an earlier IRG (International Research Group on wood Protection) paper a methodology was presented on how to present the variation in natural durability (Van Acker *et al.* 2010a). This paper intends to use this methodology for thermally modified timber as was similarly presented at the 5th European conference on Wood Modification in Riga (Van Acker *et al.* 2010b). For assessment of variability the fungal decay test data were fit to a Weibull distribution (Van Acker *et al.* 2011). Probability density functions were fitted using rank regression on X (RRX) as data were not censored. Based on three different test statistics a two-parameter (2P) Weibull distribution (Eqn. 1) was chosen as best fitted distribution in general.

$$F(ML) = \frac{\beta}{\eta}\left(\frac{ML}{\eta}\right)^{\beta-1} e^{-\left(\frac{ML}{\eta}\right)^{\beta}} \qquad (1)$$

Analyses were performed in the statistical package Weibull ++9 (Reliasoft).

The durability classification according to CEN/TS 15083-1 (2005) is based on the highest median mass loss determined for all the test specimens exposed to each of the test fungi. Unfortunately, according to EN350 this can be incorrect if high variability in results is present. Furthermore, the median value was introduced to eliminate the impact of outliers on the mean value. However, this can allow for considerable amount of values showing higher mass losses than are linked to the assigned durability class. Hence, additional information about the spread of individual mass loss values can be useful. If individual mass loss values are distributed over two durability classes (x and y) with at least 40 % of values being in each of them, the retained durability class should not be based on the median mass loss but expressed as falling between "x – y ". High levels of variability should be clearly mentioned in the test report, e.g. by "v". When over 10 % of the replicates exist, which differ from the assigned batch durability class by more than one class then the letter "v" shall be appended to the class number to indicate the variability.

RESULTS AND DISCUSSION

Using the limit value of 5 % mass loss and based on the median values, all four sets of TMT Fraké can be classified as very durable when considering the Basidiomycetes results (Table 1). This corresponds to durability class D1 according to EN 350. Reference wood species under test showed 25.5 % mass loss. When taking into account absolute mass loss values for soft rot testing (Table 2) and using the same criteria as for Basidiomycetes testing the same conclusion is possible. However when using an x-value (ratio of the median mass loss of test specimens to reference specimens) set 1 and set 2 are below, but close to the D1-D2 transition value of 0.10 while set 3 and set 4 with x-values respectively 0.21 and 0.23 should just be linked to D3. The beech reference samples showed a median mass loss of 20.1 % at the end of the soft rot test.

Table 1: Overview of statistical values of mass loss after testing according to CEN/TS 15083-1

Set	Mean	SD	Min	Max	Median	Perc 5	Perc 95
1	0.33	0.24	0.00	1.56	0.31	0.00	0.75
2	0.82	0.57	0.00	2.60	0.64	0.22	2.19
3	1.49	0.93	0.10	6.86	1.27	0.59	3.71
4	1.70	1.02	0.22	7.23	1.41	0.77	3.72

Table 2: Overview of statistical values of mass loss after testing according to CEN/TS 15083-2

Set	Mean	SD	Min	Max	Median	Perc 5	Perc 95
1	1.64	0.74	0.02	6.06	1.59	0.67	2.86
2	2.42	1.86	0.00	7.66	1.77	0.27	5.56
3	4.60	2.09	0.86	10.04	4.19	1.92	9.11
4	5.59	3.92	0.00	22.35	4.56	2.07	14.45

The four sets clearly differ in variability as indicated by standard deviation and maximum values. The fact that the mean values differ from the median values also refer to variation.
Taking into consideration the 5 % lowest mass losses (5 percentile value, Perc 5) sets 1 and 2 seem to be different from sets 3 and 4. The 5 percent highest mass losses as indicated by the 95 percentile value (Perc 95) provides most insight in the variability. The Perc 95 values for the Basidiomycetes test (Table 1) show all four sets are belonging to D1 while when using the same criteria for soft rot testing (Table 2) only set 1 can be considered fully belonging to the highest durability class D1. Set 2 and 3 show significant mass losses higher than the limit value 5 % and for set 4 there are some mass losses close to or even above the 15 % mass loss.

Both Figures 1 and 2 show Weibull probability density functions of mass losses for basidiomycetes testing and soft rot testing respectively. Although low mass losses were recorded after fungal testing with *Trametes versicolor* still one can easily observe set 1 is a far more homogeneously modified set of timber than set 4 and that the other 2 are showing intermediate variability (Figure 1). Although nearly all individual specimens can be assigned to durability class D1 there are some specimens showing over 5 % mass loss as can also be seen from the maximum values in Table 1.

In Figure 2 a fitted Weibull probability density function is fitted to the soft rot data of the four sets. Seemingly, the ranking is similar as for the Basidiomycetes fungal test. When considering 2.0 % mass loss as a criterion for D1 (beech reference mass loss of 20%), all four sets show that at least 50 % of the material is belonging to a durability class linked to a shorter service life. In Table 3 an overview is given of the percentage of actual specimens that can be assigned to different durability classes based on their mass loss after soil soft rot testing in comparison with the reference beech. According to the rules to indicate variability as stipulated in EN 350 set 4 should be indicated as D3v and set 3 as D2-D3.

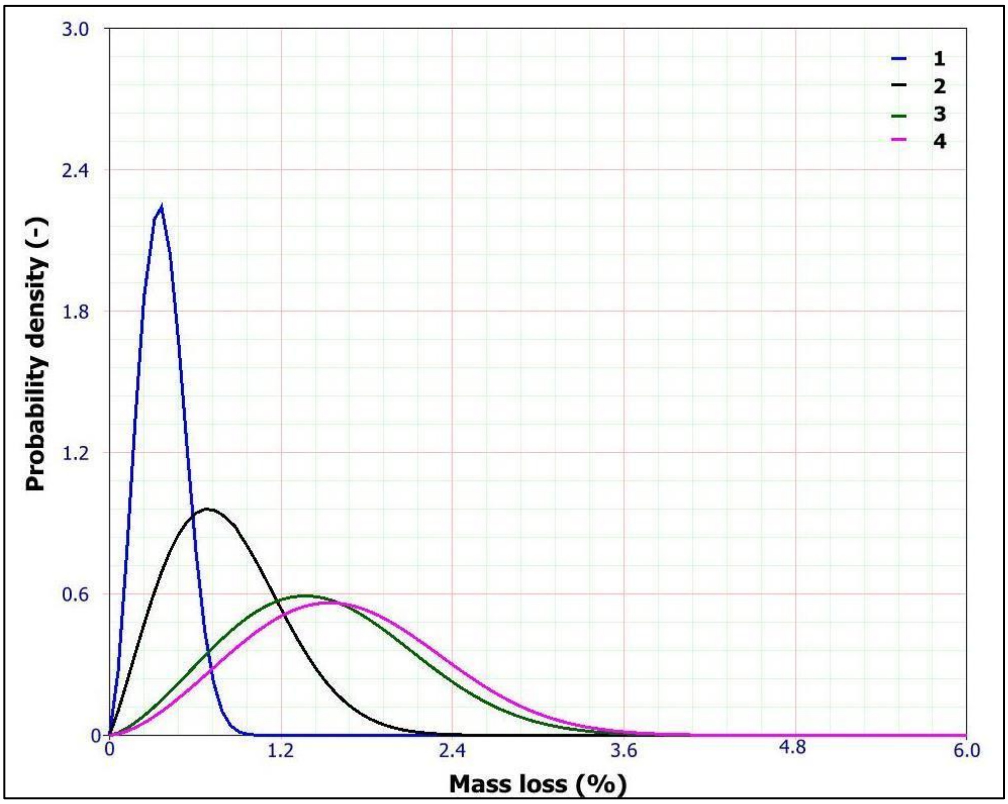

Figure 1: Weibull probability density functions of mass losses after Basidiomycetes testing (Trametes versicolor) for the four sets of TMT Fraké (see Table 1)

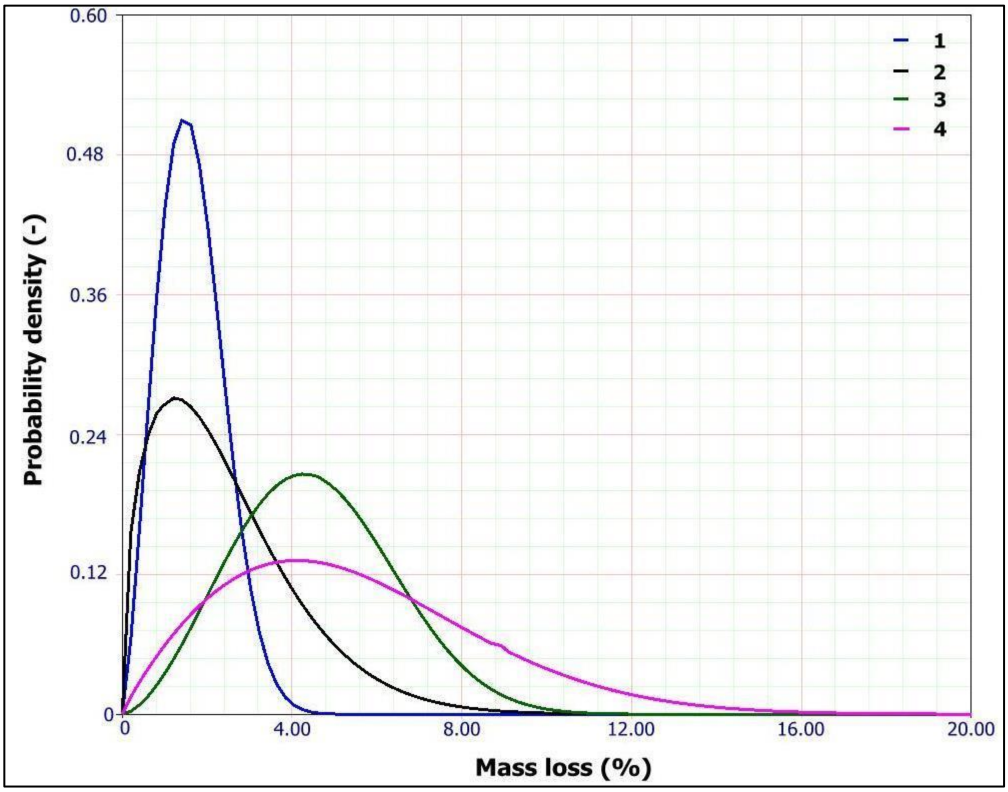

Figure 2: Weibull probability density functions of mass losses after soft rot testing for the four sets of TMT Fraké (see Table 2)

Table 3: Assigning specimens to durability classes after testing according to CEN/TS 15083-2

Set	% D1	% D2	% D3	% D4	% D5	x-value
1	78.5	20.7	0.8	-	-	0.08
2	54.2	25.8	20.0	-	-	0.09
3	5.5	41.7	47.3	5.5	-	0.21
4	4.4	34.2	46.4	11.4	2.6	0.23

CONCLUSIONS

The four different sets are related to commercial thermal modification processes and all referred to as TMT Fraké and seemingly aiming at the same durability target. Fact that considerable differences are observed with regard to variability in durability underpins the potential to limit this by selecting specific processing technology to lower potential early failure of part of the modified material. Although all four sets were considered very durable when tested against *Trametes versicolor* the classification after soft rot testing showed more differences though the same ranking as well as similar variability.

ACKOWLEDGEMENT

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Thermovuoto thermal modification of eight European wood species

Ignazia Cuccui[1], Nasko Terziev[2], Giovanna Bochicchio[1] and
Ottaviano Allegretti[1]

[1]CNR - IVALSA (National Research Council - Trees and Timber Institute), via Biasi 75, 38010 San Michele all Adige, Italy, (e-mail: allegretti@ivalsa.cnr.it)

[2]Department of Forest Products, Swedish University of Agricultural Sciences, Box7008, 75007 Uppsala, Sweden, (e-mail: nasko.terziev@slu.se)

Keywords: colour, durability, equilibrium moisture content, mass loss, mechanical strength, thermo-vacuum treatment

ABSTRACT

The paper reports some of the conclusive results of the TV4NEWOOD project, aimed promoting the use of European wood species thermally modified by means of the Termovuoto Technology (TV).

Silver fir (*Abies alba* Mill.), **spruce** (*Picea abies* Karst.), **maritime pine** (*Pinus pinaster* Aiton), **douglas fir** (*Pseudotsuga menziesii (*Mirb)Franco), **ash** (*Fraxinus* spp.), **beech** (*Fagus sylvatica* L.), **poplar** (*Populus* spp.) and **oak** (*Quercus petraea* Liebl.) 32-mm planks were treated at different process conditions and characterized. About 40 boards x species x process were treated and characterised according to EN technical standards.

Modification processes were performed in controlled laboratory condition at temperatures from 160 to 220°C, constant pressure (25 kPa) and exposure time (3 h) and two rates of temperature increase (5 and 15°C/h). Treated and untreated samples were characterised and compared regarding physical and mechanical properties, colour and durability.

The mass loss was the main indicator of the thermal degradation, influenced mainly by the temperature but also by the other process parameters. Most of the measured properties were significantly correlated to the ML. As expected, a relevant improvement of wood durability was achieved only at treatment temperatures equal or higher than 210ºC.

In general, the results confirmed that Thermovuoto process caused lower mass loss than “traditional” superheated steam thermal modification methods at identical treatment temperature and duration.

INTRODUCTION

TV is a technology for thermal modification of wood developed by CNR-IVALSA (Italy). It is characterised by an atmosphere of partial vacuum (150 mbar, O_2: 1,5%), convective heat transfer by means of high efficiency fans. It is classified as a dry process in an open system. The TV4NEWOOD project developed TV processes for commercially available European species for high quality products as substitutes of some imported tropical species. The TV technology has been already introduced in Europe and USA market. More detail can be found in different previous paper (Allegretti *et al*. 2012; Ferrari *et al*. 2013; Sandak *et al*. 2015).

RESULTS AND DISCUSSION

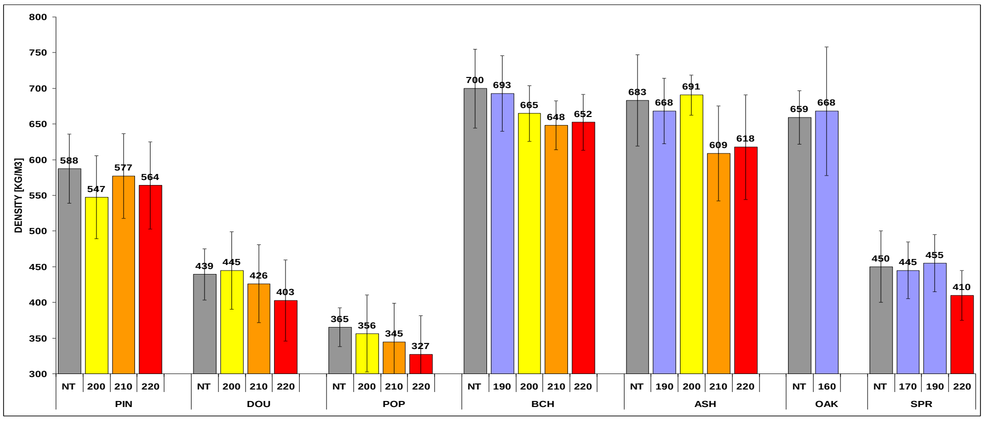


Figure 1: Measured density (average and standard deviation) of wood equilibrated at 20° C, RH 65%. (Fir and spruce are grouped together since they have the same values)

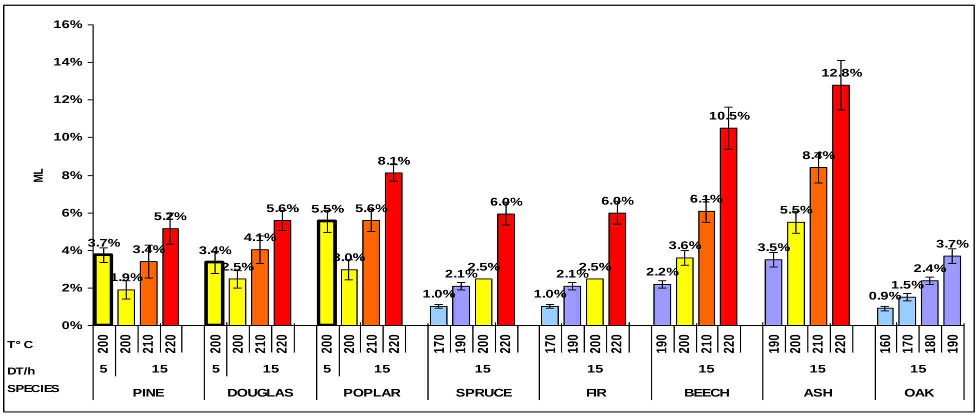


Figure 2: Measured ML (average and standard deviation)

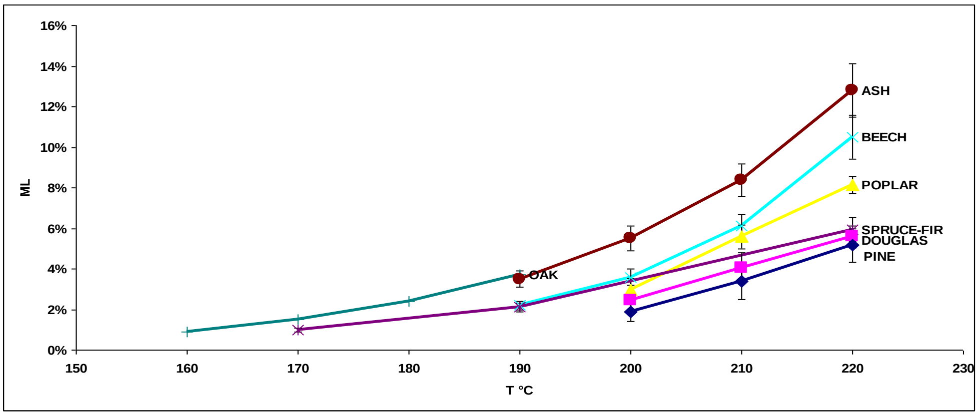


Figure 3: ML VS. T_{pr} (at constant rate of T increase of 15 °C/h and constant pressure p = 250 mbar)

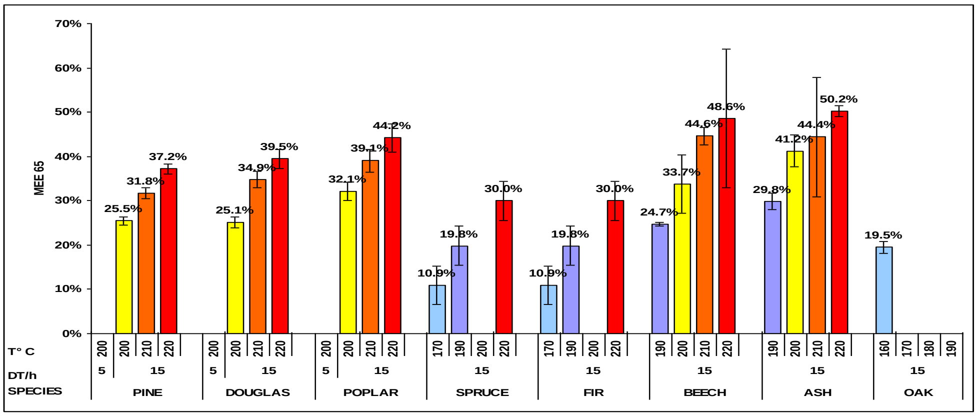


Figure 4: MEE (Moisture Exclusion Efficiency = (EMC$_{NT}$ - EMC$_{HT}$)/EMC$_{NT}$).

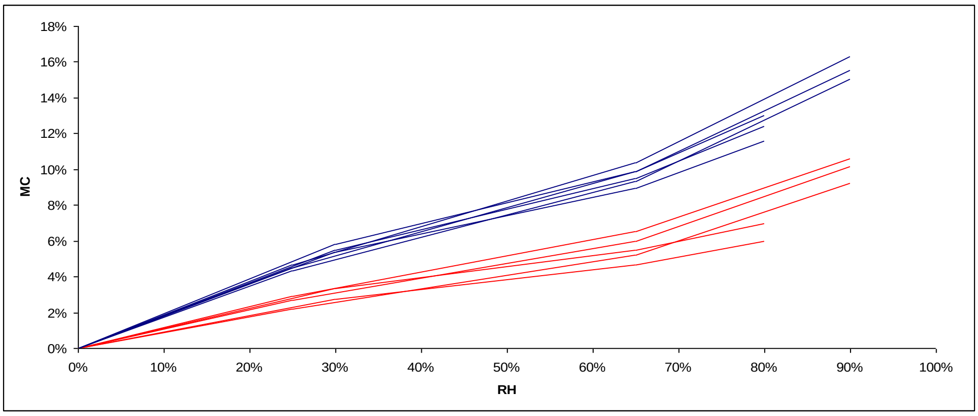
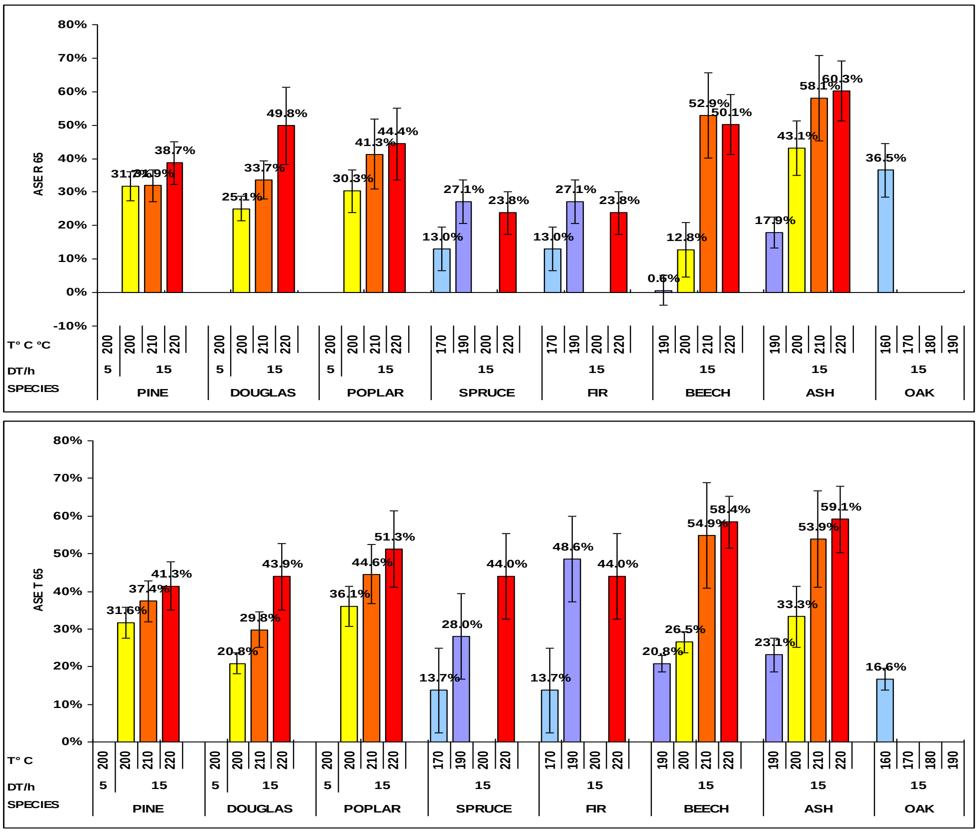


***Figure 5: Sorption curves for all species. Comparison between not treated (blu lines)** and treated (red lines).*



Figures 6 and 7: Measured ASE R and ASE T (average and standard deviation)

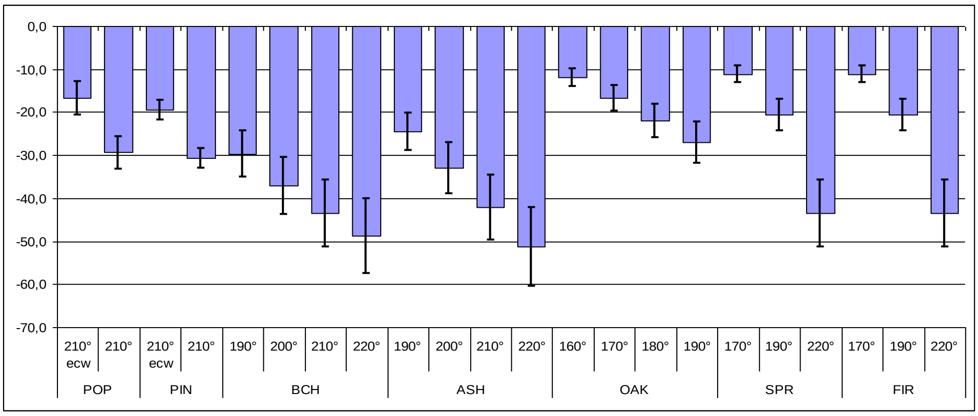


Figure 8: Colour coordinate ΔL*(average and standard deviation).

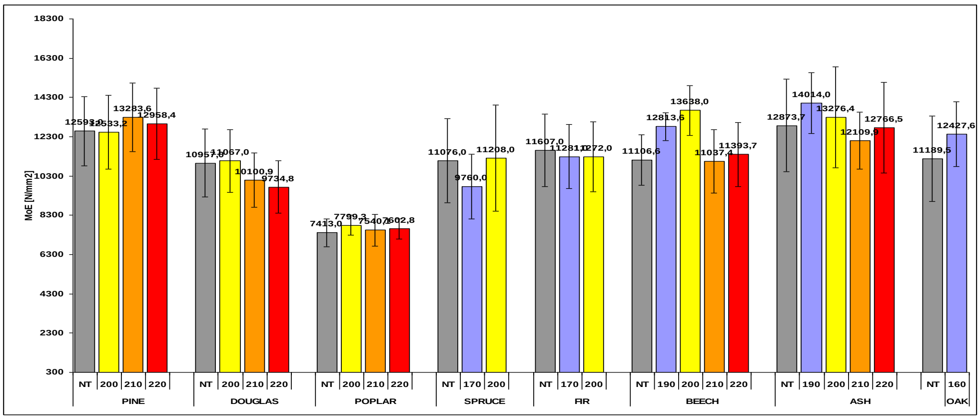


Figure 9: Bending MOE (average and standard deviation).

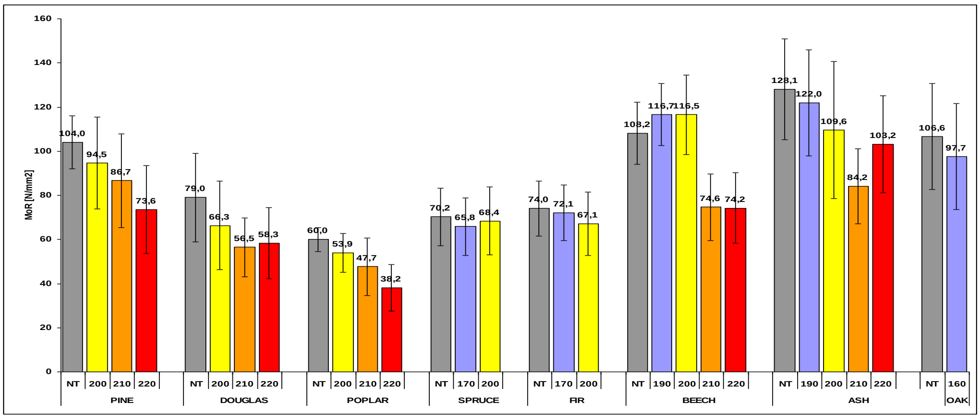
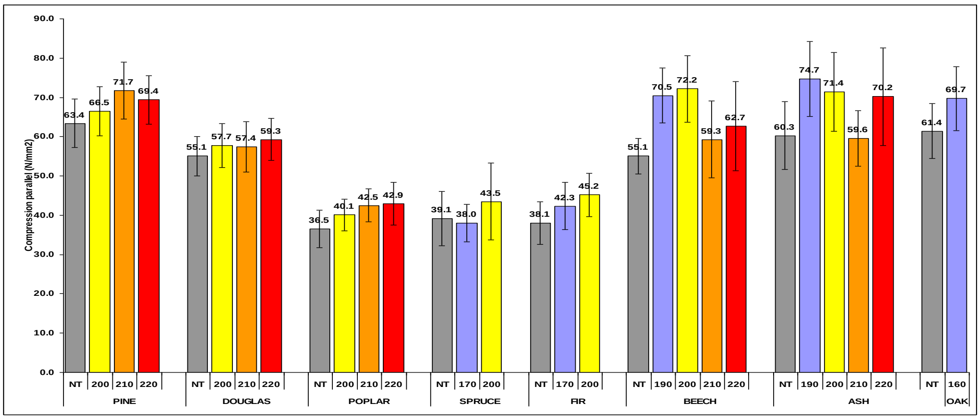
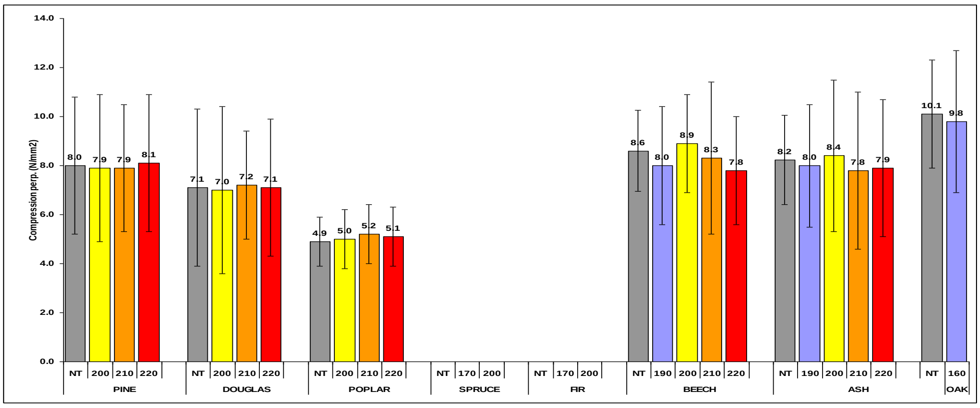


Figure 10: Bending MOR (average and standard deviation).





Figures 11 and 12: Compression parallel and perpendicular to grain (average and standard deviation).

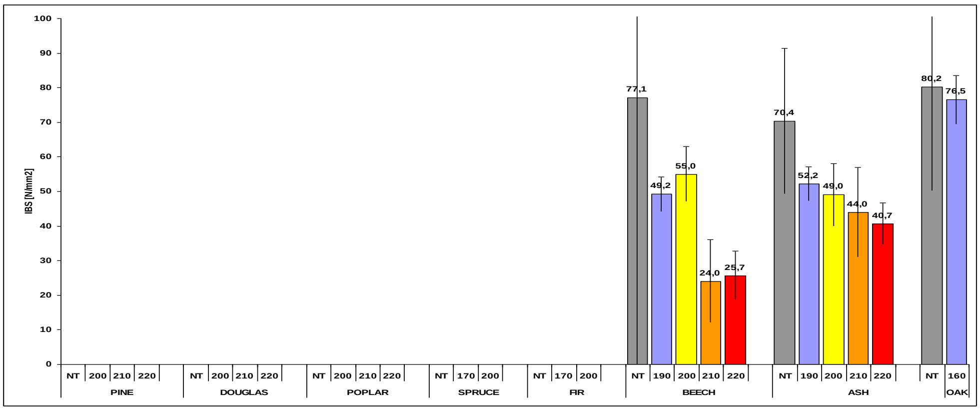
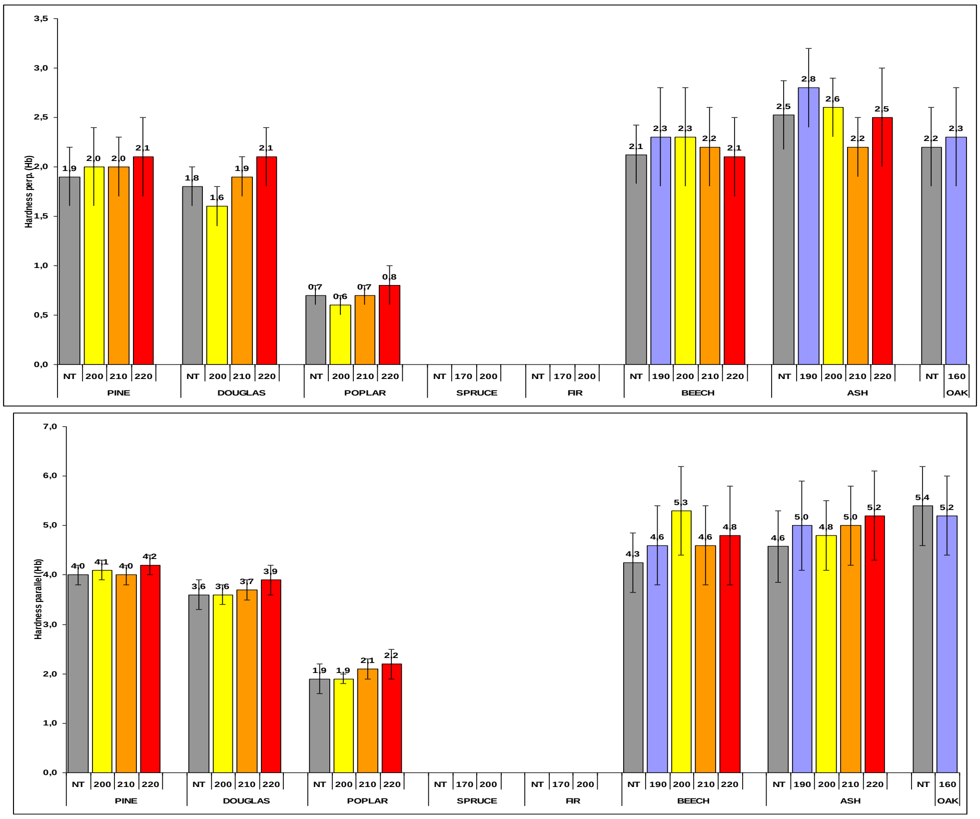


Figure 13: Average impact bending strength, average and standard deviation (missing species are due to a sampling problem).



Figures 14 and 15: Brinell hardness perpendicular and parallel to grain (average and standard deviation)

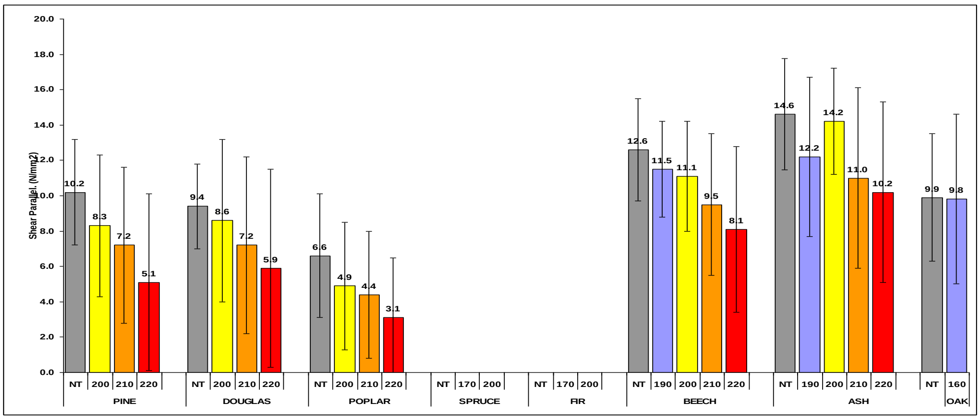


Figure 16: Shear strength parallel to grain (average and standard deviation).

Table 1: Average mass loss, correction values (%) and durability class (the red digit) of thermally modified wood leached according to EN 84. The green fields indicate treatment temperature improving the durability class.

Wood species	Fungi	Treatment temperature, °C 160	190	200	210	215	220	NT
Correction values for poplar				*0,2*	*0,15*		*0,15*	
Poplar	*Postia placenta,*			37,6 4	32,9 3		18,7 3	52.5
	Con, puteana			6,8 2	0,5 1		0,5 1	35
	Tram, versicolor			24,5 4	18,2 3		7,1 2	37.3
	Gl, trabeum			4 2	3,5 2		1,6 1	39.7
Correction values for Maritime pine				*0,1*	*0,1*		*0,1*	
Maritime pine	*Postia placenta*			30,7 4	22,8 3		26,5 3	45.6
	Con, puteana			5,7 1	1,4 1		0,7 1	41.3
	Tram, versicolor			5,9 3	2,6 2		1,5 1	15.2
	Gl, trabeum			13,9 3	3,7 1		0,8 1	29.2
Correction values for Douglas fir				*0,1*	*0*		*0,1*	
Douglas fir	*Postia placenta*			27,3 4	20,5 3		22,3 3	40.7
	Con, puteana			9,5 2	2,1 1		2,3 1	24.4
	Tram, versicolor			7,3 3	5,3 2		6,2 2	4.1
	Gl, trabeum			1,6 1	1,7 1		1,9 1	9.2
-								
Fir	*P.placenta*						8,8±6,6 2-3	40,6±7,9 -
	C. puteana						2,0±3,2 1	55,2±4,4 -
	T.versicolor						1,2±1,3 1	23,5±5,1 -
	G.trabeum						0,26±0,14 1	32,5±9,2 -
Spruce	*P.placenta*						12,8±3 3-4	35,9±7,5 -
	C. puteana						3,72±4,8 1-2	56,3±5,4 -
	T.versicolor						3,2±4,2 1-3	24,8±7,7 -
	G.trabeum						0,25±0,16 1	36,1±8,7 -
Correction values for beech			*1*	*0,9*	*1*	*0,4*	*0,6*	
Beech	*Postia plac,*		30,3 5	25,4 5	8,6 2	0,5 1	0,8 1	32.3
	Con, puteana		37,8 5	35,1 5	0,6 1	0,6 1	1,3 1	47.4
	Tram, versicolor		27,6 5	28,5 5	17,7 4	14,5 3	13,5 3	26.3
	Gl, trabeum		10,3 4	7,2 4	2,7 1	1 1	1,1 1	34.1
Correction values for ash			*1,5*	*0,9*	*1*	*0,6*	*0,7*	
	Postia plac,		30,1 5	20,1 3	3,9 2	4,7 1	1,8 1	21.4
-	*Con, puteana*		8 2	2,2 1	0,5 1	2,4 1	0,8 1	17
Ash	*Tram, versicolor*		24,1 4	19,1 4	9,8 3	4,8 3	6,7 3	18
-	*Gl, trabeum*		11,3 3	7,2 2	0,1 1	0 1	0,1 1	8.1
Correction value for oak		*2,7*						
Oak	*Postia plac.*	34,7 (5) 3-4						2.5
	Con. puteana	15,5 (5) 3-4						0.9
	Tram. versicolor	32,8 (5) 3-4						1
	Gl. trabeum	0,8 (5) 3-4						9.3

The process temperature is an evident factor influencing the residual **hygroscopicity** (Figures 4 and 5) which is reduced in the range between 15 and 50%. **Dimensional stability** (Figures 6 and 7) is increased up to 60%. For the same temperature softwood seems to be subjected to a lower variation compared to hardwood. For most species an improvement of dimensional stability of 50% is given with a ML of 5-6%.

Colour coordinate L*it is demonstrate a reliable parameter to indicate the treatment intensity (Figure 8).

Statistically significant increase of **MOE** compared to untreated samples after treatment at 190° and 200° C was found. Further increase of the treatment temperature to 210° and 220° C ensured elasticity that was similar to that of untreated samples (Figure 9). **MOR** is more sensitive to thermal treatments than the MOE. In general, the obtained results (Figure 10) are in line with the findings of other authors, e.g. show a good correlation with the findings of Allegretti *et al*. (2012).

The applied thermo-vacuum treatments have evident effect on the **compression parallel** to grain (Figure 11); all tested wood species demonstrated significantly higher compression strength. Similar results were obtained for beech and ash tested previously. The above is in line with the findings of Boonstra *et al*. (2007). The **compression perpendicular** to grain did not change significantly for the tested species and temperatures (Figure 12).

The **IBS** decreased significantly for all tested species at temperature of treatment higher or equal to 190ºC (Figure 13). IBS uses to be extremely sensitive to any changes in wood structure changed by modifications or biodegradation. It often does not correlate too well to the wood mass loss, e.g. low mass loss can result in severe decrease of IBS.

A tendency of increased **hardness** with increased treatment temperature was found (Figures 14 and 15).

Shear strength parallel to grain in tangential plane was reduced significantly after any thermo-vacuum treatment and despite the treatment temperatures (Figure 16); such a behaviour is reported previously for a number of treated wood species. For instance, Boonstra *et al*. (2007)

Durability: The untreated control specimens showed mass loss in the range demanded by the standard, i.e. more than 20% for all tested fungi; this characterises the entire test as valid. Correction value shows the change of mass due to leaching. Bi-products of thermal modification, mainly acetic acid, mono-and oligosaccharides, are easily leached after 2 weeks exposure in water.

Apparently there is significant variation in the test results caused by the various treatment temperatures and test fungi. Growth of the brown rot fungus *Con. puteana* caused smallest mass loss for all three wood species. Thermal modification (TM) at temperature of 210°C decreased the mass loss of the samples to 0.5-2.1% and thus, improved the durability of the test species to class 1, i.e. very durable when exposed to *Con. puteana*. The action of the brown rot fungus *Gl. trabeum* is similar to that of *Con. puteana* by showing that a treatment temperature of 210°C ensures low mass loss of 1.7-3.7% for the softwoods and 3.5% for poplar. Accordingly, the durability for Maritime pine and Douglas fir is shifted to class 1 (very durable) and class 2 (durable) for poplar. The white fungus *Tram. versicolor* demonstrated a gradual decrease of its ability to degrade wood with increased treatment temperature. Thermal treatment at 200°C ensures durability class 3 or 4 while the treatment at 220°C improved further the durability class for the softwoods to class 1 and class 2 for Poplar. The most aggressive fungus on the tested TM wood was the brown rot *P. placenta*. This is in line with data available in the literature and. durability tests on Spruce and Fir performed also in the scope of the project. *P. plac*enta caused an average mass loss of 18.7% (Poplar), 26.5 (Maritime pine) and 22.3% (Douglas fir) even after treatment at 220°C and thus, classified the wood of the three tested species in class 3.

Poplar is the wood species with improved durability after treatment at 210°C from class 5 to class 3 when tested to *P. placenta* and *T. versicolor* and even durability classes 1 or 2 to the other two fungi. Maritime pine and Douglas fir showed improved durability after treatment at 210°C to all fungi (durability classes 1 or 2) except *P. placenta* (durability class 3). Although the treatment temperature was elevated to 220°C, *P. placenta* was able to cause significant mass loss on the softwoods and thus, only durability class 3, i.e. moderately durable was reached. Oak is already in durability class 3-4 and it is a refractory species and when treated at T > 160°C is undergone to severe internal crack and collapse. The durability of oak decreased from the expected class 3-4 according to the standard to class 5 (perishable). This can be attributed to thermal destruction of some extractives that leach out (2.7%, while the wood polymers are not altered drastically due to the low temperature (160°C). The test results confirm that a temperature of at least 210°C is needed to improve significantly the durability of wood and to achieve the durability class 3 needed to use the wood in the risk class 3: exterior exposed to rain.

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Differences in the mechanical behaviour of wood after thermal modification in oven-dry or water-saturated state

Michael Altgen[1], Tuuli Uimonen[2] and Lauri Rautkari[3]

[1]Department of Bioproducts and Biosystems, School of Chemical Engineering, Aalto University, P.O. Box 16300, FI-00076 Aalto [email: michael.altgen@aalto.fi]

[2]Department of Bioproducts and Biosystems, School of Chemical Engineering, Aalto University, P.O. Box 16300, FI-00076 Aalto [email: tuuli.uimonen@aalto.fi]

[3]Department of Bioproducts and Biosystems, School of Chemical Engineering, Aalto University, P.O. Box 16300, FI-00076 Aalto [email: lauri.rautkari@aalto.fi]

Keywords: 3-point bending; Chemical composition; Compression parallel to the grain; Thermally modified wood

ABSTRACT

The loss in strength and ductility of wood during the thermal modification is a major drawback that hinders its use in load-bearing applications. Up until today, the link between the chemical changes during the thermal modification and the changes in the mechanical behaviour is still not fully understood. This study aims at separating the effect of depolymerisation of cell wall polymers (i.e. hemicelluloses) and the effect of the formation of additional cross-links in wood during the thermal modification process on its mechanical behaviour. This is achieved by comparing the thermal modification of water-saturated wood in pressurized hot water at mild temperatures (≤170 °C) with the thermal modification of oven-dry wood in a superheated steam atmosphere at elevated temperatures (≥180 °C). Analysis of the chemical composition evidenced that both modification processes caused the preferential removal of hemicelluloses. However, additional repolymerisation reactions during the modification of dry wood caused an overestimation of the lignin percentage and an underestimation of the hemicellulose percentage based on the obtained mass loss. In contrast, the partial depolymerisation of lignin resulted in the overestimation of the hemicelluloses percentage based on the mass obtained by the modification of wood in water-saturated state. The bending strength and strain energy density of wet thermally modified wood decreased along the depolymerisation sequence that was reported previously. This verifies the role of hemicelluloses as coupling agents for the transfer of stresses over the cell wall as a continuum. However, a higher lignin percentage and enhanced cross-linking in dry thermally modified wood resulted in an additional reduction in strength, strain energy density and ductility. This was assigned to the prevention of inelastic deformation during bending that hindered compression yielding and caused a brittle tension failure in the dry modified wood. The results suggest the role of hemicellulose depolymerisation in causing a brittle failure in bending to be smaller than suggested previously.

INTRODUCTION

Thermal modification is applied on industrial-scale for more than two decades to prolong the service life of wood by increasing its dimensional stability and biological durability. However, this property change induced by cell wall changes during the exposure to heat is accompanied by a loss in strength and ductility (Kubojima *et al.* 2000; Boonstra *et al.* 2007). The latter may cause problems in load-bearing applications. Mechanical behaviour of thermally modified wood is often determined in quasi-static three-point bending tests. During such tests, compression stresses develop at the top of the sample and tensile stresses in the material at the opposite region, while shear stresses occur in the neutral zone, where the bending stresses become zero. For small and defect-free samples of unmodified wood, the tensile strength usually exceeds the compression strength, which results in distinct compression yielding with pronounced inelastic deformation during bending (Buchanan 1990). Besides reducing the bending strength, thermal modification results in a large loss in strain energy (area below the stress-strain curve), while the stiffness remains almost unchanged. The magnitude of these changes are strongly dependent on the modification temperature and duration applied and are linked to chemical changes in the wood cell wall (Boonstra *et al.* 2007).

During thermal modification, amorphous hemicelluloses are preferentially degraded, resulting in the increase in the content of crystalline cellulose and lignin in the wood residue (Kollmann and Fengel 1965). Hemicelluloses are expected to act as coupling agents that enable the transfer of stresses over the cell wall as a continuum. Thus, their preferential removal is assumed to be the major factor in reducing the strength and toughness of thermally modified wood (Hughes *et al.* 2015; Winandy 2017). Winandy (2017) hypothesized that the loss in strength loss during heat-exposure proceeds in the order of: (1) hydrolytic depolymerisation of side-chain hemicelluloses, which is followed by (2) the hydrolytic depolymerisation of the main chain hemicelluloses, and only at high strength loss levels by (3) the depolymerisation of cellulose and/or lignin.

Although this depolymerisation sequence is not only applicable to the strength loss caused by heat-exposure, but also to the loss in strength by chemical treatments or biological decay (Winandy 2017), it does not consider the contribution of repolymerisation reactions to the change in mechanical behaviour. During the thermal modification of wood, repolymerisation reactions may lead to additional covalent bonds and cross-links in the cell wall matrix of the modified wood. Ester bond formation (Tjeerdsma and Militz 2005; Liang and Wang 2017) or condensation reactions between the lignin and furan-type derivatives derived from the degradation of hemicelluloses (Inari *et al.* 2007), are likely pathways for such enhanced cross-linking. These repolymerisation reactions are likely to affect the mechanical behaviour of thermally modified wood in addition to the effect of depolymerisation of cell wall polymers. However, this effect is often overlooked, because de- and repolymerisation reactions are interrelated and occur simultaneously, thereby hindering the separation of their individual impact.

This study attempts to separate the effect of de- and repolymerisation reactions during thermal modification on the mechanical behaviour of Scots pine (*Pinus sylvestris* L.) sapwood by applying two different modification methods to the wood. Thermal modification of oven-dry wood at temperatures between 180 and 240 °C in superheated steam at atmospheric pressure was applied to facilitate cross-linking within the cell wall matrix. In contrast, thermal modification of water-saturated wood in pressurized hot water at temperatures between 120 and 170 °C was applied to favour hydrolytic depolymerisation of cell wall polymers. The mechanical behaviour of the modified wood was evaluated by testing three-point bending and compression parallel to the grain. Analysis of the chemical composition was performed on the same material.

EXPERIMENTAL

Material

Kiln-dried boards of Scots pine sapwood were cut to samples with dimensions of 13×13×180 mm^3 (R×T×L) and 23×23×110 mm^3 (R×T×L). All samples were free of heartwood, knots and visible defects. All samples were oven-dried using a temperature sequence of 40, 60, 80 and finally 103°C, with each temperature being held for ca. 24 h, for the determination of the initial dry mass.

Thermal modification processes

For the thermal modification in dry state (TM$_{dry}$) the samples were kept in a desiccator over silica gel until the treatment. TM$_{dry}$ was performed in an oven with continuous insertion of superheated steam by increasing the temperature stepwise by 15 °C every 30 min starting from an initial temperature of 105 °C until reaching the target maximum temperature. Treatments with maximum temperatures of 180, 195, 210, 225 and 240 °C were applied for 3 h and then the oven temperature was decreased to >100 °C.

For the thermal modification in wet state (TM$_{wet}$), the samples were vacuum-impregnated (50 mbar for 1 h) with deionized water approx. 24 h before the treatment. The samples were placed in closed vessels with a volume of 2.5 l together with deionized water in a solid to liquid ratio of 1:20 (g/g). The vessels were heated to the maximum temperature at a rate of ca. 55 °C h^{-1} in an air bath digester while rotating slowly. Treatments with maximum temperatures of 120, 130, 140, 150, 160 and 170 °C were applied for 2 h, before the vessels were removed from the air bath digester and placed in a cold water bath under continuous water flow for 30 min.After the thermal modification processes, all samples were leached with deionized water for 14 days with daily water changes. Reference samples and samples treated by TM$_{dry}$ were vacuum impregnated with deionized water prior to the water leaching. After the leaching, the samples were oven-dried by applying the temperature sequence described above to determine the final dry mass and calculate the mass loss (in %) caused by thermal modification.

Chemical composition

Samples tested in three-point bending were milled in a Wiley mill to pass through a 30 mesh screen and extracted in a Soxhlet apparatus with acetone. Determination of carbohydrates and lignin was performed according to the analytical protocol NREL/TP-510-42618 (Sluiter *et al.* 2012). Carbohydrates were determined by High Performance Anion Exchange Chromatography with Pulse Amperometric Detection (HPAEC-PAD) in a Dionex ICS-3000 column. The acid-soluble lignin was determined in a Shimadzu UV-2550 spectrophotometer using a wavelength of 205 nm and an absorptivity constant of 110 L g^{-1} cm^{-1}. The acid-insoluble fraction was determined gravimetrically after drying at 103 °C for 12 h. The lignin percentage was calculated as the sum of the acid-soluble and the acid-insoluble fraction. Hemicellulose percentage was calculated as the sum of all detected monosaccharides except glucose. All samples were analysed in duplicate. The results are given as ratios with the value of the unmodified reference set to 1.

Mechanical testing

All samples with initial dimensions of 13×13×180 mm^3 and 23×23×110 mm^3 were conditioned at 20°C and 65% RH and then processed to samples with dimensions of 10×10×180 mm^3 (for bending tests) and 20×20×30 mm^3 (for compression tests), respectively. The bending test was conducted with 15 replicates per sample group (treatment process and maximum temperature) on a universal testing machine (Zwick 1475) equipped with a 20 kN load cell and combined with a MTS Premium Elite controller. The span length was set to 150 mm and the load was applied in the tangential direction at a rate of 3 mm min^{-1}. Deflection (δ, in mm) was set to zero at a load (P, in N) of ca. 4 N. Bending strength (MOR, in N mm^{-2}) was defined as the maximum stress. Modulus of elasticity (MOE, in N mm^{-2}) was determined as the slope of a linear regression curve of the stress-strain curve within the range between 10 and 40 % of MOR. Strain energy density (u, in kJ mm^{-3}) was computed as the area below the stress-strain curve up to the strain at maximum stress (ε_{max}; in mm mm^{-1}). Elastic strain ($\varepsilon_{elastic}$) and elastic strain energy density ($u_{elastic}$) were calculated according to Eqn. 1 and Eqn 2.

$$\varepsilon_{elastic}=MOR/MOE \qquad (1)$$

$$u_{elastic}=MOR\times(\varepsilon_{elastic}/2) \qquad (2)$$

Brittleness was quantified by the brittleness index (BI, in %) that was calculated based on Eqn. 3.

$$BI=100\times(u_{elastic}/u) \qquad (3)$$

The compression test parallel to the grain was conducted with 18 replicates per sample group on the same universal testing machine, but with a 100 kN load cell. The load was applied in the longitudinal direction at a rate of 1 mm min^{-1}. Displacement (in mm) was set to zero at a load (P, in N) of ca. 30 N. Maximum stress was defined as compression strength (CS, in N mm^{-2}). The specific gravity (in kg mm^{-3}) of all samples was determined by relating the volume in conditioned state to the respective dry mass. By dividing MOR, u and CS by the specific gravity, the specific MOR (MOR_{spec}; in N mm kg^{-1}), the specific strain energy density (u_{spec} in kJ kg^{-1}) and the specific CS (CS_{spec}, in N mm kg^{-1}) were computed for each sample. MOR_{spec}, u_{spec} and CS_{spec} are given as ratios with the value of the unmodified reference set to 1.

Scanning electron microscopy

Samples treated by TM_{dry} at 240 °C and samples treated by TM_{wet} at 170 °C, with bending properties close the group average were selected for the investigation of the fracture surface by scanning electron microscopy (SEM). Small cross-cuts with a length of ca. 40 mm were taken from the bending samples for SEM observations. The samples were dried at 50 °C and <100 mbar for 24 h and sputter-coated with gold-palladium, before the observation in a Zeiss Sigma VP SEM (Oberkochen, Germany). The observation was limited to the tension side of the fracture surface.

RESULTS AND DISCUSSION

Chemical changes

Both modification techniques resulted in the preferential removal of hemicelluloses and an accumulation of lignin and cellulose in the wood residue. The presence of excessive amounts of water during TM_{wet} caused a very efficient removal of wood mass, which lead to a larger mass loss by TM_{wet} at 170 °C for 2 h (25.2 %) than by TM_{dry} at 240 °C for 3 h (14.1%). This is caused by the catalytic effect of hydronium ions formed by water auto-ionization, and the formation of acetic acid that accumulates in the process water during TM_{wet} (Garrote *et al.* 1999). However, there are differences in the compositional changes as a function of mass loss, which are a consequence of the shift from the preferential hydrolytic depolymerisation during TM_{wet} to additional repolymerisation during TM_{dry}. Figure 1 shows the lignin and hemicellulose ratios as a function of the mass loss caused by the modification process. The increase in lignin by TM_{wet} is lower than calculated when assuming that mass loss is solely caused by carbohydrate removal, which evidences a partial depolymerisation and removal of lignin. In contrast, the increase in lignin by TM_{dry} is larger than calculated. Furan-type derivatives (i.e. furfural and HMF) are formed by the dehydration of hydrolysed hemicelluloses. Repolymerisation reactions that involve such degradation products and the lignin add to lignin percentage that is determined using the analytical protocol applied (Inari *et al.* 2007). Such repolymerisation is also one potential pathway for the creation of additional cross-links within the cell wall matrix of dry thermally modified wood.

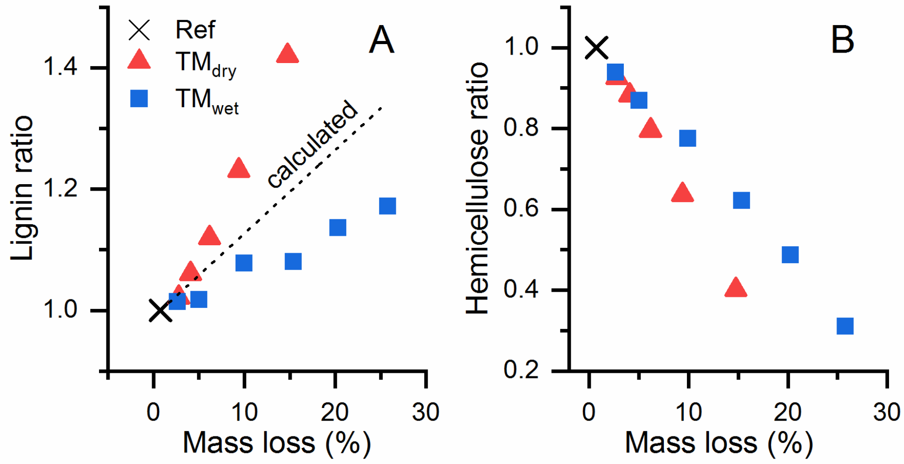

Figure 1: Lignin ratio (A) and hemicellulose ratio in dependence on the mass loss caused by thermal modification. The dotted line in (A) represents the theoretical lignin ratio that is calculated based on the assumption that mass loss is solely caused by carbohydrate removal.

Differences in the extent of de- and repolymerisation reactions also affect the decrease in hemicellulose ratio (Figure 1 B). The degradation of hemicelluloses is overestimated based on the mass loss in case of TM_{wet}, because removal of lignin partially contributes to the mass loss. In contrast, mass loss underestimates the degradation of hemicelluloses during TM_{dry}, because the hemicellulose degradation products partially remain within the wood due to their involvement in repolymerisation reactions. However, the analysis of the different monosaccharides found in the wood hydrolysates (data not shown) evidenced the same temperature-dependent depolymerisation sequence for both modification processes: monosaccharides found primarily at the side chains (arabinose and galactose) were removed more rapidly during thermal modification than monosaccharides that built the main chain of the hemicelluloses (mannose and xylose).

Mechanical properties

Thermal modification decreases the density of the wood, thus stresses are distributed over less cell wall material. This density effect was removed from the data by analysing specific values that are related to the respective specific gravity of each sample. Changes of these specific values can be directly assigned to changes in chemical composition and in the structural arrangement of the cell walls.

Since the MOE_{spec} ratio remained nearly constant, except for a small decrease to 0.87 at after TM_{wet} at 170 °C, the data is excluded from the analysis. Figure 2 shows the changes in MOR_{spec}, u_{spec} and BI as a function of the hemicellulose ratio. If the depolymerisation of hemicelluloses during the thermal modification was the only factor that determines the change in mechanical behaviour, no differences between TM_{wet} and TM_{dry} would be expected. However, the two modification processes differed strongly in their impact on the mechanical behaviour of the wood. After TM_{wet}, MOR_{spec} and u_{spec} decreased linearly with decrease hemicellulose ratio, in line with the presumed impact of hemicellulose depolymerisation on the strength and toughness of wood (Hughes et al. 2015; Winandy 2017). Remarkably, the effect of TM_{dry} on MOR_{spec} and u_{spec} as a function of the hemicellulose ratio was much stronger than the effect of TM_{wet}.

Especially in case of u_{spec}, the decrease became non-linear, which indicates that the depolymerisation of hemicelluloses was not the only cause for the change in mechanical behaviour by $\mathrm{TM}_{\mathrm{dry}}$.

The difference in the mechanical behaviour between the two modification processes was most noticeable for the BI. $\mathrm{TM}_{\mathrm{wet}}$ resulted in a slight increase in BI with decreasing hemicellulose ratio to a maximum of 55 %. Even for hemicellulose ratios as low as 0.78, the BI almost remained compared to the reference value of 41 %. However, at the same hemicellulose ratio, a BI above 80% was reached by $\mathrm{TM}_{\mathrm{dry}}$ and a BI of 95 % was determined after $\mathrm{TM}_{\mathrm{dry}}$ at 240 °C, which demonstrates that the material failed almost without any inelastic deformation.

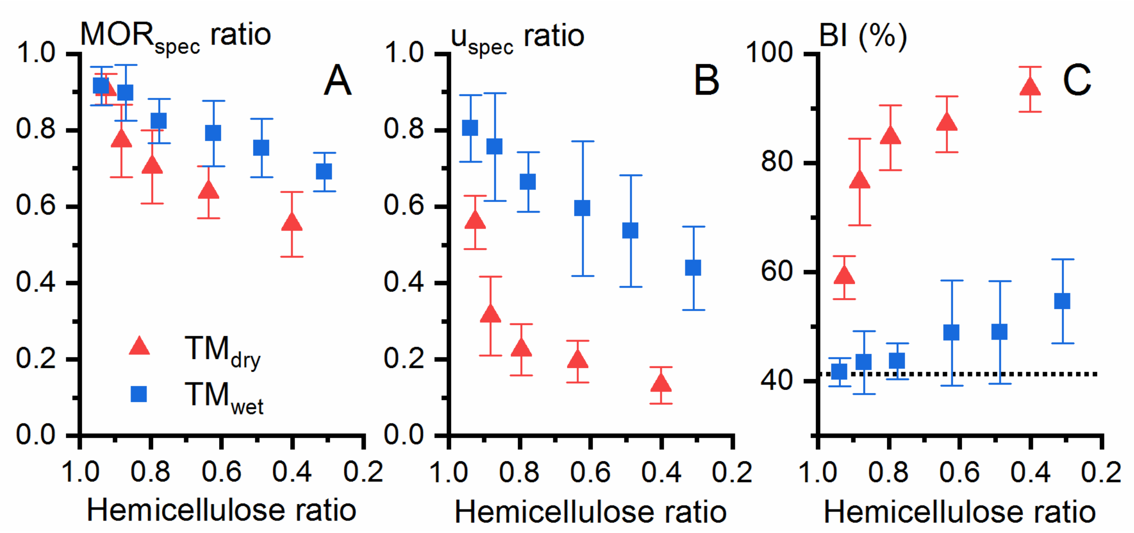

Figure 2: Results of the three-point bending test in dependence on the hemicellulose ratio. (A) Specific bending strength ratio, (B) specific strain energy density ratio and (C) brittleness index (in %; C). The dotted line in (C) represents the average BI of the reference samples. (±95 % confidence interval)

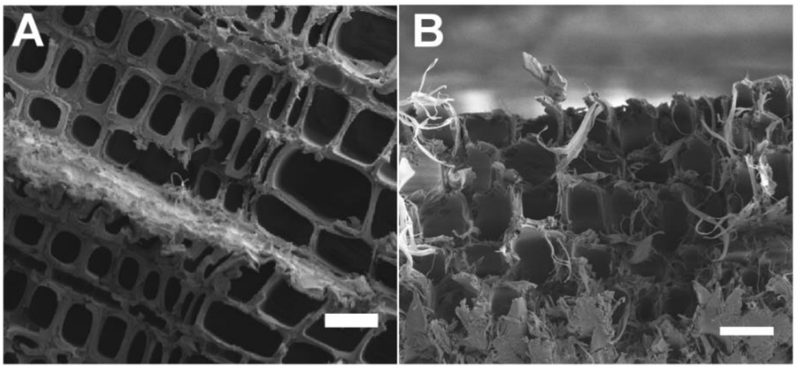

Figure 3: SEM images of the fracture surface of the bending test samples taken on the tension side. (A) $\mathrm{TM}_{\mathrm{dry}}$ at 240 °C; (B) $\mathrm{TM}_{\mathrm{wet}}$ at 170 °C. (Scale bar = 30 µm)

The differences in the mechanical behaviour were also clearly visible in the SEM observation of the fracture surfaces (tension side) of selected bending samples (Figure 3). After $\mathrm{TM}_{\mathrm{dry}}$ at 240°C, the fracture surface was very flat and the cell wall appeared as if cut by a razor blade. Such a fracture is typical for the brittle failure of dry thermally modified wood (Boonstra et al. 2007). In contrast, a more ragged fracture surface with fibril structures sticking up from the cell wall was observed after $\mathrm{TM}_{\mathrm{wet}}$ at 170°C.

The differences in the bending test results between the two modification processes can be explained by an additional restriction in inelastic deformation of the dry modified wood compared to the wet modified wood. A loss in inelastic deformation leads only to a small loss in strength, because the increase in stress as a function of strain is comparably low in the inelastic region. However, a loss in inelastic deformation causes a large reduction in strain energy density and ductility, in line with the differences between TM_{wet} and TM_{dry} shown in Figure 2. Inelastic deformation requires the rearrangement of the cell wall polymers by plastic flow. This might be partly reduced by a higher percentage of lignin, which forms a rigid network in the cell wall, in dry compared to wet modified wood. However, strong differences in the bending behaviour are already evident at mild modification intensities, where differences in the lignin percentage are comparably low. As discussed in detail in previous studies (Altgen *et al.* 2016, 2018), TM_{dry} also results in a more facile formation of cross-links within the cell wall than TM_{wet}, which are likely to further reduce the inelastic deformation under bending loads

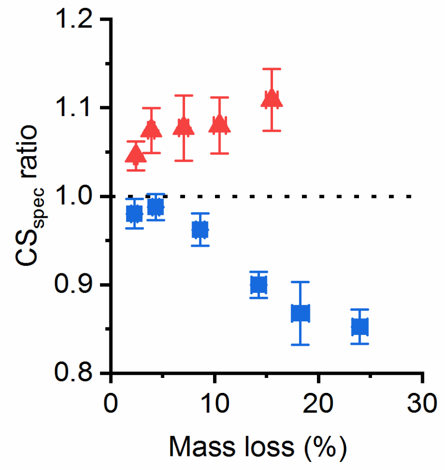

Figure 4: Specific compression strength in dependence on the mass loss. (±95 % confidence interval)

In unmodified wood, the inelastic deformation originates mostly from compression yielding at the top of the sample (Buchanan 1990). In line with the conclusion of a hindered inelastic deformation in bending by additional cross-linking, TM_{dry} increased the CS_{spec} ratio with increasing mass loss (Figure 4), which prevents compression yielding during bending to cause a brittle tension failure. In contrast, the CS_{spec} ratio decreased by TM_{wet}, thereby enabling inelastic deformation by compression yielding even at large levels of hemicellulose depolymerisation.

CONCLUSIONS

The strength and strain energy density of wood that was thermally modified in water-saturated state at mild temperatures (≤170°C) in pressurized hot water, decreased along the depolymerisation sequence reported previously. However, thermal modification of dry wood at elevated temperatures (≥180°C) in superheated steam resulted in an additional reduction in strength and strain energy density, which was assigned to the effect of cross-links within the wood cell wall matrix that are formed during the modification of dry wood. Additional cross-links in the cell wall matrix of dry thermally modified wood hindered the compression yielding to cause a brittle tension failure during bending. The lack of cross-linking during the thermal modification in water-saturated state enabled inelastic deformation by compression yielding even at high levels of hemicellulose removal.

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Thermal modification of wax impregnated wood

Miha Humar[1]*, Davor Kržišnik[1], Boštjan Lesar[1], Nejc Thaler[1], Aleš Ugovšek[2], Gregor Rep[3]

[1] University of Ljubljana, Biotechnical Faculty, Department of Wood Science and Technology, Jamnikarjeva 101, SI1000, Ljubljana, Slovenia [email: miha.humar@bf.uni-lj.si; davor.krzisnik@bf.uni-lj.si; bostjan.lesar@bf.uni-lj.si; nejc.thaler@bf.uni-lj.si]

[2] M SORA d.d., Trg svobode 2, SI4226 Žiri, Slovenia [email: ales.ugovsek@m-sora.si]

[3] Silvaprodukt d.o.o., Dolenjska c. 42, SI1000 Ljubljana, Slovenia [email: gregor.rep@silvaprodukt.si]

Keywords: contact angle (CA), durability classes, DSC, water uptake, mechanical properties, natural wax, thermal modification

ABSTRACT

Thermally modified wood has improved durability but, predominately in moist conditions, its performance does not meet expectations, predominately due to low moisture performance. In order to reduce water uptake of modified wood, Norway spruce (*Picea abies*) specimens were dipped and vacuum-pressure treated with a suspension of natural wax. Wax treated specimens were subsequently thermally modified at four temperatures (185°C, 200°C, 215°C and 230°C). Control specimens were heated up to 100°C only. Contact angle, short-term and long-term water uptake and bending strength were determined. The results showed that a combination of wax treatment and modification resulted in a synergistic effect that considerably improved hydrophobicity and reduced liquid water uptake of the treated material.

INTRODUCTION

Thermally modified wood performs well in less exposed applications, in which the wood is not exposed to liquid water too often (e.g. façades). If thermally modified wood is used in ground contact or severe above ground application (use class 3.2 or higher according to EN 335 (CEN, 2013), with many moisture traps, then the performance of thermally modified wood does not meet the specifications of the producers (Brischke *et al.*, 2015). Field studies with moisture monitoring of thermally modified wood (especially if modified to higher degrees) revealed that such wood uptakes a lot of water, which leads to the development of favourable conditions for fungal, and sometimes even for bacterial growth (Van Acker *et al.*, 2015). Several alternatives are therefore being investigated of how to improve the performance of thermally modified wood in more demanding applications. Salman *et al.* (2014) investigated the application of various biocidal solutions that make modified wood toxic to fungi. We believe that this is not in line with the idea of an environmentally friendly approach to modifying wood. The aim of this study was to improve moisture performance (and consequently performance against fungal growth) with a combination of wax treatment and thermal modification.

Wax can be applied to wood in melted form (Brischke and Melcher, 2015), diluted in an organic solvent or in the form of emulsions or suspensions (Lesar and Humar, 2014). The main advantage of suspensions is that impregnation can take place at lower temperatures, in less complicated autoclaves and less wax is applied. In order to make a wax treated surface hydrophobic, the surface of wood must be heated above the wax melting point (Lesar *et al.*, 2011). Under these circumstances, wax on the surface can act as a semi-permeable membrane, which prevents liquid water uptake and enables water vapour diffusion. Hence, wax treatment does not influence the equilibrium moisture content of the wood, only slows down water vapour diffusion. Since wax requires heating above melting point, the wax was applied prior to wood modification in order to make this process more economic. The main aim of this study was to determine the performance of wax treated and subsequently thermally modified wood against wood decay fungi and moisturizing. In parallel, the mechanical properties of wax-treated modified wood were also determined.

EXPERIMENTAL

Samples were made of Norway spruce (*Picea abies*) since this wood species is one of the most important materials used in construction applications in Europe. Specimens were cut to final dimensions prior to impregnation. All specimens were made from the same plank. The wood was free of visual signs of defect and discolouration. Prior to further processing, samples were conditioned under laboratory conditions.

A commercial natural wax emulsion was used for impregnation. The commercially available concentrated emulsion was diluted with deionised water to achieve 2.5% and 5.0% dilutions of the original formulation. Two impregnation processes were tested: 30 min of immersion (dipping procedure) and vacuum-pressure impregnation (10 MPa, 3 h). Vacuum-pressure impregnation was performed according to the full-cell process in a laboratory impregnation setup (Kambič, Slovenia). Uptakes were subsequently determined gravimetrically. Impregnated specimens were conditioned for two weeks prior to thermal modification. Non-impregnated specimens were used as controls.

The thermal modification was performed in a laboratory kiln according to the Silvapro® commercial procedure (Rep *et al*., 2012). Samples were thermally modified at four temperatures (185°C, 200°C, 215°C and 230°C). Control specimens were only heated up to 100°C for 24 h during the drying procedure. The time of modification at the target temperature was 3 hours and mass loss of the samples after the modification was determined gravimetrically. After modification, samples were stored in the laboratory for 4 weeks (23°C; 65%). The conditioned samples were then subjected to various tests.

The sessile drop method was used to determine the contact angles (CA) of distilled water on the surfaces of the specimens (25_T mm × 15_R mm × 50_A mm) with a Theta (Optical Tensiometer) from Biolin Scientific Oy, Espoo – Finland. Droplets of 4 µl were applied at three different locations on each specimen. The measurements were taken at a constant temperature of 21°C. For each treatment, three measurements were performed on five specimens (15 average measurements/treatment).

Short-term water uptake was measured according to the modified EN 1609 (CEN, 1997) procedure, using a tensiometer device (Krüss Processor Tensiometer K100MK2) at room temperature, 23°C, and at RH of 65 ± 5%. The uptake was measured from the axial surfaces; the mass of partially immersed (0.5 mm) samples was recorded every two seconds for a period of 200 seconds. The result was given as mass of water uptake per immersed area of the specimen (g/mm^2). Short-term water uptake measurements were performed on five replicate specimens.

In order to determine long-term liquid water uptake, 125 specimens (5 replicates/treatment) were prepared. Conditioned specimens were immersed in distilled water (all surfaces exposed, no end seal) and the mass of the specimens was determined prior to immersion, after 1 h and after 24 h of immersion. The results are presented as moisture content (the initial mass is the dry mass of treated specimens before exposure to water).

Modulus of elasticity (MoE) and modulus of rupture (MoR – bending strength) were determined according to the EN 310 (CEN, 1993) procedure, with a static three-point bending test on a Zwick Z005 universal testing machine (Zwick-Roell). In total, 175 test specimens (7 parallel specimens for each treatment/25 different treatments) with dimensions 100_A mm × 20_T mm × 5_R mm were prepared and oven dried (103°C; 24 h) prior to testing. Samples were oven dried, in order to equalize moisture content of thermally modified specimens.

DSC measurements were performed on the high-pressure differential scanning calorimeter HP DSC 1 (Mettler Toledo) with pined 40-μl aluminium crucibles was used for DSC measurements. The first sample of air-dried wax emulsion, with a mass of 24.75 mg, was heated from 25°C to 350°C at a heating rate of 10 K/min. The second sample of air-dried wax emulsion, with a mass of 8.21 mg, was preheated at 120°C for 1 hour, cooled down and then heated up again from 25°C to 350°C at a heating rate of 10 K/min. Analysis of the wax was performed in a dynamic nitrogen atmosphere under normal pressure (100 kPa).

RESULTS AND DISCUSSION

Two impregnation procedures were applied in this experiment: immersion and vacuum-pressure treatment. Retention of wax was determined gravimetrically. This value represents the amount of wax and additives that remained in the wood after impregnation. As expected, full cell impregnation (7.79 kg/m^3) resulted in much higher uptakes than achieved by the immersion procedure (1.19 kg/m^3) (Table 1). After impregnation, samples were thermally modified. Samples modified at 185°C lost on average 2.4% of the initial mass, and the specimens modified at 230°C lost 11.3% of initial mass (Table 1). Wax treatment prior to modification does not have a major influence on a mass loss. Statistical analysis does not prove any influence of wax impregnation on mass loss after thermal modification. This was also confirmed by the DSC studies.

The DSC analysis consists of two thermograms representing the melting process of preheated and non-preheated wax. Our observations suggest that the wax-heating process consists of several endothermic reactions. Not-preheated wax had two initial endothermic peaks, at 42°C and 59°C, followed by a broader endothermic reaction with two peaks, at 106°C and 121°C. The latter two peaks were not present after the wax was preheated at 120°C for 1 hour but the initial peaks were present at very similar temperatures (44°C and 61°C). Thermal decomposition of the analysed wax did not occur in the temperature range up to 350°C.

Table 2: Average retention of waxes and mass losses after thermal modification determined with Norway spruce wood specimens. Standard deviations are expressed in brackets.

Wax concentration (%)	Impregnation procedure	Modification temperature (°C)	Wax retention (kg/m^3)	Mass loss after modification (%)
0	/	100	/	0.06 (0.00)
		185	/	2.11 (0.24)
		200	/	5.34 (0.39)
		215	/	5.78 (0.86)
		230	/	10.01 (1.66)
2.5	**Dipping**	100	0.90 (0.24)	0.04 (0.00)
		185	0.81 (0.31)	1.91 (0.19)
		200	0.81 (0.29)	4.61 (0.56)
		215	0.88 (0.18)	6.76 (0.81)
		230	0.76 (0.22)	12.40 (2.03)
	Vacuum-pressure	100	6.77 (0.46)	0.03 (0.00)
		185	6.59 (0.34)	2.61 (0.33)
		200	7.09 (0.56)	5.16 (0.46)
		215	7.42 (0.39)	6.78 (0.68)
		230	7.34 (0.31)	9.8 (1.57)
5.0	**Dipping**	100	1.58 (0.39)	0.05 (0.00)
		185	1.90 (0.55)	2.29 (0.40)
		200	1.46 (0.47)	4.37 (0.66)
		215	1.35 (0.51)	6.97 (1.04)
		230	1.41 (0.56)	13.46 (2.61)
	Vacuum-pressure	100	8.28 (1.62)	0.04 (0.00)
		185	7.73 (1.17)	2.86 (0.30)
		200	8.61 (0.84)	5.26 (0.50)
		215	8.76 (1.75)	7.36 (0.44)
		230	9.26 (1.16)	11.00 (0.73)

Contact angle (CA) is one of the parameters that clearly indicate the surface properties of wood. The data presented in Table 2 shows that even untreated Norway spruce has a fairly hydrophobic surface. The CA determined on spruce was 123.6° after 1 s, and it then slightly decreased to 116.1° after 55 s. The thermal modification did not result in increased contact angles. Wang *et al.* (2015) reported similar observations on the southern yellow pine. The CA of spruce modified at the highest temperature was 114°. Wax impregnation improved the hydrophobicity of spruce wood, as is evident from the CA determined on wood. If dipping and vacuum-pressure treatment are compared, a less prominent effect was noted with specimens that were dipped into wax solution prior to modification. A more prominent effect of wax on the contact angle was observed with specimens that were vacuum-pressure impregnated prior to modification. The most hydrophobic surfaces were determined with specimens that were heated up to 100°C or thermally modified at the lowest temperature of 185°C. Furthermore, contact angles determined on the surface of wax treated and thermally modified spruce remained constant during the 55 s of measurements (Table 2).

Table 3: Influence of wax concentration, impregnation method and modification temperature on water contact angle on the surface of Norway spruce specimens. Standard deviations are given in the brackets.

Wax concentration (%)	Impregnation procedure	Modification temperature (°C)	Time of contact between droplet and wood (s)		
			1	10	55
			Contact angle (°)		
0	/	100	123.6 (9.4)	119.9 (10.2)	116.1(10.7)
		185	119.4 (6.1)	118.3 (6.3)	114.5 (4.9)
		200	114.3 (2.3)	113.4 (2.2)	112.0 (2.2)
		215	112.4 (3.6)	109.5 (4.7)	108.2 (5.2)
		230	114.8 (2.3)	113.1 (2.6)	110.7 (2.6)
2.5	**Dipping**	100	127.2 (5.5)	127.2 (5.6)	126.9 (5.6)
		185	125.9 (4.2)	125.8 (4.2)	125.3 (4.1)
		200	122.2 (2.7)	121.6 (3.0)	120.4 (2.7)
		215	121.2 (5.0)	121.5 (5.7)	120.3 (5.0)
		230	112.8 (3.9)	112.3 (4.0)	110.7 (4.5)
	Vacuum-pressure	100	130.4 (6.7)	130.1 (6.4)	129.8 (6.4)
		185	132.1 (4.2)	131.8 (3.9)	131.4 (3.9)
		200	131.5 (4.4)	131.6 (4.7)	131.2 (4.7)
		215	122.7 (5.5)	122.7 (5.7)	122.2 (5.7)
		230	123.5 (6.3)	123.4 (6.7)	122.9 (6.4)
5.0	**Dipping**	100	132.4 (6.4)	132.0 (6.2)	131.5 (6.3)
		185	132.1 (6.1)	132.1 (6.0)	131.5 (6.1)
		200	122.0 (6.0)	118.7 (10.3)	118.1 (10.4)
		215	125.5 (3.3)	125.1 (3.2)	124.7 (3.3)
		230	105.9 (8.8)	105.6 (9.1)	104.4 (8.7)
	Vacuum-pressure	100	130.9 (5.8)	130.7 (5.4)	130.6 (5.8)
		185	131.2 (4.8)	131.0 (5.1)	130.6 (5.1)
		200	129.7 (5.7)	129.6 (5.7)	129.3 (5.7)
		215	122.7 (9.3)	122.3 (9.5)	121.5 (9.2)
		230	123.5 (3.4)	123.4 (3.3)	123.0 (3.3)

Short-term water uptake measurements take slightly longer (200 s) than contact angle measurements (55 s). However, they indicate different parameters and reflect properties on different planes. CA measurements were determined on tangential/radial planes, while short-term water uptakes were determined only on the axial planes. The highest short-term water uptake after 200 s was determined with control wood (0.157 g/cm^2), while specimens modified at 230°C performed best (0.045 g/cm^2). Similar results have been reported in previous studies (Humar *et al.*, 2014). Wax treatments were surprisingly effective, regardless of the subsequent modification temperature. The spruce wood tracheids were completely blocked with wax, preventing any liquid water uptake, which resulted in minimal (even negative) values of water uptake (Table 3).

A quite good correlation existed between short-term and long-term water uptake since both are based on capillary water uptake. Water uptake was determined after several periods, between 1 hour and 72 hours; however, only results after 1 h and 24 h are reported. Similar to short-term water uptake, higher degree of modification resulted in lower water uptakes. The MC of control specimens after one hour of immersion was 28.5%, while a considerably lower MC was determined after one hour of immersion of specimens modified at 230°C; only 7.4%. A similar influence of modification temperature was also determined after 24 h of immersion. This is in line with previous laboratory observations (Pfriem *et al.*, 2010). A combination of wax and thermal modification performs synergistically on long-term water uptake. The concentration of wax and the method of wax impregnation did not have a significant influence on water uptake. The influence of wax treatment on reduced MC during long-term water uptake was more evident with specimens modified at lower temperatures than with specimens modified at higher temperatures. Higher modification temperatures, in any case, make wood hydrophobic, so there is less room for improvement. A positive effect of wax treatment on the decrease of water uptake was also evident after 24 hours of immersion (Table 3). The positive effect of wax was visible in both control and at modified specimens.

Table 4: Influence of wax treatment and thermal modification on short term (tensiometer) and long-term water uptake determined after 1 h and 24 hours of dipping. Standard deviations are expressed in brackets.

Wax concentration	**Impregnation procedure**	**Modification temperature (°C)**	**Short term water uptake (g/cm^2)**	**MC after 1 h of immersion (%)**	**MC after 24 h of immersion (%)**
0	/	100	0.157 (0.073)	28.50 (0.10)	55.12 (0.13)
		185	0.095 (0.057)	13.48 (0.06)	47.62 (0.11)
		200	0.120 (0.058)	10.28 (0.03)	51.90 (0.16)
		215	0.062 (0.055)	8.43 (0.02)	42.73 (0.13)
		230	0.045 (0.026)	7.43 (0.00)	39.79 (0.08)
2.5	**Dipping**	100	-0.004 (0.003)	9.92 (0.00)	27.13 (0.02)
		185	-0.006 (0.004)	7.77 (0.00)	23.33 (0.01)
		200	-0.005 (0.007)	7.92 (0.00)	24.16 (0.01)
		215	-0.005 (0.005)	7.18 (0.01)	21.57 (0.02)
		230	0.002 (0.012)	6.21 (0.00)	18.69 (0.01)
	Vacuum-pressure	100	-0.018 (0.023)	14.72 (0.26)	29.54 (0.29)
		185	-0.013 (0.009)	8.28 (0.14)	20.21 (0.14)
		200	-0.016 (0.014)	3.54 (0.16)	15.54 (0.17)
		215	-0.038 (0.010)	5.17 (0.00)	16.51 (0.02)
		230	-0.013 (0.002)	4.98(0.00)	15.27 (0.01)
5.0	**Dipping**	100	-0.019 (0.009)	8.78 (0.00)	24.76 (0.02)
		185	-0.013 (0.010)	7.30 (0.00)	23.29 (0.01)
		200	-0.008 (0.006)	6.46 (0.00)	21.20 (0.01)
		215	-0.005 (0.004)	5.91 (0.00)	19.35 (0.01)
		230	-0.005 (0.005)	5.99 (0.00)	20.08 (0.01)
	Vacuum-pressure	100	-0.011 (0.005)	8.68 (0.01)	23.80 (0.03)
		185	-0.006 (0.004)	6.54(0.00)	20.09 (0.00)
		200	-0.006 (0.005)	6.02(0.00)	19.27 (0.01)
		215	-0.012 (0.009)	5.56(0.00)	17.87 (0.00)
		230	-0.006 (0.004)	5.03 (0.00)	15.63 (0.01)

Mechanical properties are another important parameter in potential applications of modified wood. In order to avoid the influence of MC on the bending strength and modulus of elasticity, specimens were oven dried before testing. Conditioning in a standard climate would result in various MC due to various degrees of modification. As generally accepted (Militz and Altgen 2014), bending strength and modulus of elasticity decreases with increasing modification temperature. This was also evident from our experiment (Table 5). This phenomenon is well explained and discussed in the literature (Welzbacher and Scheiding, 2011; Militz and Altgen, 2014). Due to the fairly high variability of the specimens, it is very difficult to reach conclusions. In general, wax treatment did not decrease mechanical properties.

Table 5: Modulus of elasticity and bending strength of wax treated and thermally modified Norway spruce wood specimens. Standard deviations are expressed in brackets.

Wax concentration (%)	Impregnation procedure	Modification temperature (°C)	MoE (N/mm²)	Bending strength (N/mm²)
0	/	100	11384 (2535)	128.9 (23)
		185	10289 (2716)	97.1 (33)
		200	9750 (1951)	76.3 (19)
		215	9852 (2486)	80.1 (25)
		230	8058 (2863)	51.6 (23)
2.5	**Dipping**	100	9585 (2339)	99.4 (24)
		185	8969 (2346)	79.1 (20)
		200	9123 (2235)	70.5 (21)
		215	8741 (2364)	64.5 (22)
		230	10339 (2325)	70.6 (22)
	Vacuum-pressure	100	11420 (2929)	122.3 (32)
		185	10287 (3311)	95.1 (28)
		200	10001 (3518)	81.2 (29)
		215	8975 (2338)	69.5 (21)
		230	9787 (1708)	66.7 (12)
5.0	**Dipping**	100	8024 (931)	90.8 (7)
		185	9186 (2320)	86.7 (20
		200	9508 (2512)	80.1 (23)
		215	11186 (2611)	82.2 (24)
		230	8943 (2663)	61.9 (29)
	Vacuum-pressure	100	9990 (2217)	115.2 (36)
		185	11382 (2790)	106.0 (30)
		200	11204 (2557)	99.5 (24)
		215	9997 (2528)	79.4 (28)
		230	8721 (2741)	65.4 (26)

CONCLUSIONS

Tigr4smart Wax treatment prior to thermal modification proved to be effective. DSC studies showed that the wax remained in the wood after modification. Despite fairly low quantities of wax applied, the hydrophobicity of the wood improved significantly, as determined by contact angle measurements. Furthermore, wax treatment acted synergistically with thermal modification, resulting in reduced short-term and long-term water uptakes. Wax treatment did not reduce the bending strength or modulus of elasticity. The combination of wax treatment and subsequent thermal modification provides a new material, which can overcome some drawbacks of thermally modified wood. This concept is being further tested in ongoing field trials.

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The role of accessible hydroxyl groups in reversible and irreversible EMC changes by thermal wood modification

Wim Willems[1], Michael Altgen[2], Lauri Rautkari[2]

[1]FirmoLin, Grote Bottel 7b, 5753 PE, Deurne, Netherlands [email: w.willems@firmolin.eu)]
[2] Department of Bioproducts and Biosystems, Aalto University, P.O. Box 16300, 00076 Aalto, Finland [email: michael.altgen@aalto.fi, lauri.rautkari@aalto.fi)]

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ABSTRACT

Heat treatment (HT) is a well-known means to reduce the room-temperature equilibrium wood moisture content (EMC) at a specified relative humidity (RH). Already at slightly elevated temperature above room temperature, EMC is decreased in proportion to the exposed temperature. At higher elevated temperature, where wood chemical changes become activated, the EMC is profoundly reduced, mainly caused by the loss of accessible hydroxyl groups (OH_{acc}) in the wood matrix. However, earlier experiments have shown that the obtained EMC reduction after HT can be partly reversible, depending on the ability of the wood matrix polymers to fully mechanically relax during HT. We present an experimental study on the OH_{acc} content and the associated EMC decrease at 93%RH by a relaxation inhibiting dry-HT versus a relaxation enabling wet-HT. The results of this study quantitatively support a molecular explanation of this phenomenon, in which wood moisture is principally bound by OH_{acc}-pairs, instead of solitary OH_{acc}. The irreversible part of EMC reduction is assigned to the thermochemical removal of OH_{acc} from the wood matrix. The reversible part (EMC recovery), is attributed to a regrouping of solitary OH_{acc} into pairs, thereby restoring moisture sorption sites. Each solitary OH_{acc}, may either be the remaining half of an OH_{acc}-pair after thermal destruction of its partner OH_{acc}, or originate from thermally disrupted OH_{acc}-pairs without OH_{acc} removal. The OH_{acc}-pair recovery mechanism explains the involvement of wood polymer relaxation, necessary to translocate OH_{acc} in the wood matrix.

INTRODUCTION

The equilibrium moisture content (EMC) of wood can be readily reduced by high-temperature exposure and drying, although this effect may be partly reversible, as can be verified by the application of consecutive wetting/drying cycles (Obataya and Tomita 2002, Altgen and Militz 2016). The reversibility has been ascribed by these authors to a non-equilibrium arrangement of wood polymers in the cell wall after the heat treatment (HT). The presence of crosslinks or hydrogen-bonds formed during dry-HT hinders the relaxation of the cell wall polymers towards their thermodynamically most favourable arrangement. This relaxation hinderance in HT-wood may be lifted by a post-treatment of vacuum impregnation with water or by applying consecutive cycles of wetting and drying. In the wet-HT process, polymer relaxation is accomplished during HT, avoiding or reducing the EMC recovery after the HT process (Obataya *et al*. 2002, Altgen and Militz 2016). The possibility of a (partial) EMC recovery deserves a scientific study, since the EMC is regarded as a key parameter of wood modification (Ringman *et al*. 2014).

To study the EMC recovery mechanism in more detail, Scots pine sapwood samples were prepared in a wide range of HT severities, obtained by dry heating in atmospheric superheated steam versus a hydrothermal treatment, both followed by an extraction of the water-soluble degradation products (Altgen *et al*. 2018). The OH_{acc} content was measured by hydrogen-deuterium exchange (HDX) and correlated with $EMC_{93\%}$, the EMC at first exposure to 93% RH. In this way, we could compare the $EMC_{93\%}$ at each OH_{acc} content in relatively crosslinked (dry-HT) versus soft (wet-HT) extractive-free matrices of thermally modified wood. These two extremes are considered to represent the unrelaxed state of as-produced dry heated thermally wood and the corresponding final state after full relaxation, without the potentially disturbing effect of residual degradation products in the cell walls.

The results in this paper highlight a proposed mechanism for the EMC recovery in thermally modified wood by polymer relaxation. These results are an excerpt from a larger study addressing the changes in elemental chemical composition, dry mass loss and the dimensions in the dry and fully swollen state (Altgen *et al*. 2018).

EXPERIMENTAL

Materials

Scots pine sapwood (*Pinus sylvestris* L.) was cut to dimensions of 20×20×10 (R×T×L) mm^3. The samples were clear of heartwood, knots and macroscopic defects. Fifteen replicates per sample group (treatment process and peak temperature) were used. All samples were oven-dried using a temperature sequence of 40, 60, 80 and finally 105 °C, with each temperature being held for 24h, before the initial dry mass and dimensions were determined.

Heat treatments and leaching procedure

For dry-HT, oven-dry samples were heated in an oven at atmospheric pressure with superheated steam to a peak temperature of 180, 195, 210, 225 or 240 °C, which was held for 180 minutes, before cooling the oven to room temperature. For wet-HT, the oven-dried samples were water-impregnated (50 mbar for 1h) first, and then placed in small vessels with addition of deionized water (solid:liquid 1:20 g/g). The filled, closed vessels were heated in a slow rotating air bath digester to a peak temperature of 120, 130, 140, 150, 160 or 170 °C, which was held for 120 min before cooling for 30 min under continuous tap water flow. After HT, all samples, including the reference samples, were leached with deionized water after the treatment. Dry-HT samples and reference samples were vacuum-impregnated (50 mbar for 1 h) with deionized water before leaching. Within the course of two weeks, the water was changed daily to remove the remaining degradation products. The samples were then dried carefully at ambient conditions for a minimum of one week.

Hydrogen-deuterium exchange (HDX) and $EMC_{93\%}$

OH_{acc} were quantified in a DVS apparatus (DVS Advantage ET, Surface Measurement Systems, London, UK) with a measuring accuracy of 0.1 µg and a gas flow of 200 cm^3 min^{-1} at 25 °C during the measurement. Samples that were cut from the same slat before HT were used. Approx. 15.5 (±0.3) mg of material was taken from the middle of each sample using a razor blade. This material was subjected to the following sequence: (a) a drying step under dry N_2 flow (0% RH) until the mass change per minute was less than 0.0005 % min^{-1} over a 10 min period, to determine the initial dry mass; (b) a partial pressure of 93% using a mixture of dry N_2 and deionized water for 12h, to determine $EMC_{93\%}$; (c) a drying step as described above, to remove all water; (d) a partial pressure of 86.5% using a mixture of dry N_2 and deuterium oxide (D_2O), for HDX; and finally (e) another drying step as described above, to determine the dry mass of the deuterated sample, from which the OH_{acc} content can be calculated under the assumption that each accessible OH group exchanges one ^{1}H atom for a ^{2}H atom.

RESULTS AND DISCUSSION

It is generally accepted that thermal wood modification leads to a reduction in EMC. In many textbooks and countless journal articles, the EMC reduction is ascribed to the loss of OH-groups from the wood matrix. However, quantitative experimental studies relating EMC to the content of hydroxyl groups are very scarce. The HDX method has become a major tool in determining the OH-content, since it only counts the relevant OH-groups in moisture sorption that are accessible by water molecules. However, getting reliable results from the adopted gravimetric HDX method requires a sufficient reaction time with D_2O and very accurate dry mass measurements before and after HDX. The ratio between the determined $EMC_{93\%}$ and OH_{acc} for the pine reference sample gives an occupancy of about 1 mole of water per mole of OH_{acc} at 93%RH (Figure 1, closed circle), consistent with independently estimated values for amorphous cellulose by *et al*. (1996) and for wood by Willems (2014). The found OH_{acc} content of 10.3 mmol g^{-1} for the leached pine wood control sample is somewhat larger than reported values of 9.0 mmol g^{-1} for spruce (Thybring *et al*. 2017), 7.5 to 9.5 mmol g^{-1} for radiata pine (Popescu et al. 2014), 7.5 and 8.1 mmol g^{-1} for sesendok and acacia (Rautkari et al. 2013) and 6.8 mmol g^{-1} for *Styrax tonkinensis* (Phuoung *et al.* 2007). On the other hand, similar or slightly higher OH_{acc} contents, compared to the value in the present study, have observed for unmodified pine and spruce (Kymäläinen *et al*. 2015, *et al*. 2018).

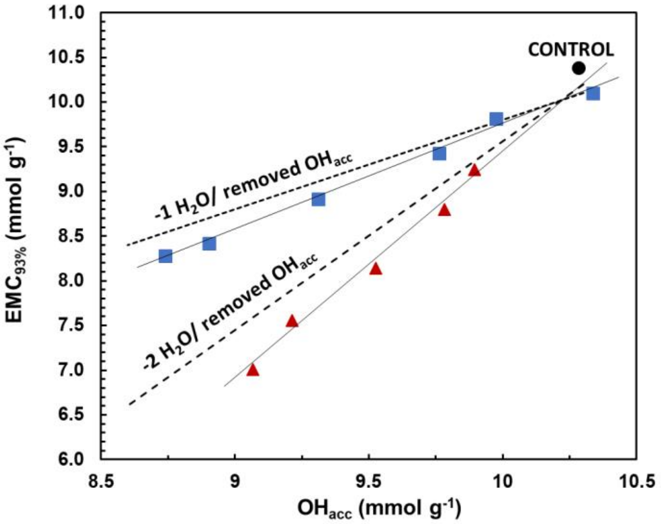

Figure 1: $EMC_{93\%}$ versus OH_{acc} content after dry-HT (triangles) or wet-HT (squares) and leaching. Control sample (circle) is leached, but not exposed to heat.

Our results (Figure 1) confirm that dry-heating causes a much larger EMC-decrease at first 93% RH exposure than hydrothermal treatment at the same modification level, as reported by Obataya *et al*. (2002) on spruce and Altgen and Militz (2016) on beech. The differences between the $EMC_{93\%}$ of dry-HT and wet-HT remain in alternative correlations with the dry mass loss or the oxygen-to-carbon atomic ratio (Altgen *et al*. 2018).

A tentative explanation of the different EMC's at the same OH_{acc} content is found in the work of Popescu *et al*. (2014) with a cell wall bulking wood modification treatment, where the volume of the incorporated bulking adduct determines the EMC reduction, rather than the associated substitution level of OH_{acc}. It could be argued that the thermal degradation products of the cell wall become covalently bonded to the cell wall as bulking adducts during dry-HT, whereas they become dissolved in the wet-HT process liquid. Such bulking would implicate a lesser dry mass loss and a larger dry dimension at the same OH_{acc} content for dry-HT samples. However, at a mass loss of 22%, we observed an equal dry dimension loss and an equal OH_{acc} content (9 mmol g^{-1}) for wet-HT and dry-HT (Altgen *et al*. 2018), whereas the $EMC_{93\%}$ clearly deviate (Figure 1).

Another tentative explanation is a crosslinking between cell wall polymers occurring in dry-HT in contrast to wet-HT. Dry-HT provides the most favourable conditions for crosslinking by condensation reactions. This would implicate that the maximum swelling by liquid water saturation would be significantly less for dry-HT compared to wet-HT, which is indeed confirmed by observations in our study and those of others (Obataya et al. 2002, Altgen *et al*. 2016, 2018). A swelling limitation could limit $EMC_{93\%}$ without effect on the measured OH_{acc}, since the conversion of OH_{acc} to OD_{acc} can proceed sequentially by dynamic occupation of all OH_{acc} by D_2O, even if these OH_{acc} cannot be simultaneously water-occupied, as in the case of cell wall bulking (Popescu *et al*. 2014; Willems 2018). Hence, this study cannot rule-out crosslinks being the reason behind the deviating linear relationship between $EMC_{93\%}$ and OH_{acc} for dry- vs. wet-HT. However, based on the observations of Obataya and Tomita (2002) and Altgen and Militz (2016), one can speculate that the $EMC_{93\%}$ of the dry-HT wood might gradually move towards that of the wet-HT wood. This would implicate that the crosslinks or hydrogen bond interactions are not lasting – which is not verified in this study.

The slope of the linear correlations between $EMC_{93\%}$ and OH_{acc} is close to 1.0 mole H_2O per removed mole of OH_{acc} for wet-HT and 2.0 for dry-HT, respectively (Figure 1). Statistical linear regression evaluations indicate significant differences from these integer values for the water occupation of the removed OH_{acc}: 1.18 ± 0.04 for wet-HT and 2.53 ± 0.15 for dry-HT. Interestingly, the ratio between the two measured slopes is an integer, equal to 2 within 1σ deviation (2.1 ± 0.2). This points at yet another possible explanation in conjunction with arguments that moisture sorption sites in wood are constituted by *pairs* of OH_{acc}, binding isolated water molecules as well as small molecular clusters of water, with thermodynamically controlled local occupation statistics (Willems 2018). For each randomly removed OH_{acc}, a sorption site is lost by the destruction of an OH_{acc}-pair. However, the remaining halves of each destructed OH_{acc}-pair may combine into a new pair, restoring one sorption site from two lost ones. The factor 2 between the slopes of Figure 1 can accordingly be explained by considering that wet-HT provides favourable conditions for wood polymer relaxation by the plasticizing effect of water, enabling the full restoration of sorption sites from isolated OH_{acc} after thermal destruction of their partner OH_{acc}. These solitary OH_{acc} would remain unpaired in dry-HT wood by a lack of relaxation. Dry-HT wood may be subject to stimulated relaxation under service conditions by cycles of wetting and drying, explaining the EMC recovery as observed by Obataya and Tomita (2002) and Altgen and Militz (2016).

The proposed EMC recovery mechanism might be speculated to play a role in the EMC losses by heating at low temperature, below the threshold of any significant wood chemical changes. OH_{acc} pairs might be disrupted without OH_{acc} removal. The EMC loss is fully recoverable by soaking in water (Thybring *et al*. 2017), promoting polymer relaxation. However, Thybring *et al*. (2017) showed that the OH_{acc} content is temporarily reduced after heating, until vacuum impregnation with water restored the original OH_{acc} content, unlike the proposed EMC recovery mechanism where the isolated OH_{acc} remain visible but are inactivated as moisture sorption sites, in absence of a partner OH_{acc}.

CONCLUSIONS

Pine wood has been thermally modified by dry heating with atmospheric steam and full-liquid hydrothermal treatment. With both heating modes and a subsequent water extraction step to remove residual degradation products, a progressive loss of accessible hydroxyl groups is achieved, responsible for an EMC reduction. The correlation between the EMC after first exposure to 93% RH and the directly measured OH_{acc} content by the gravimetric HDX method is completely different for dry- versus wet-HT.

Confirmed crosslinking in dry-HT wood might be directly responsible for the differences in the initial EMC-OH_{acc} relation, compared to wet-HT wood. These crosslinks would limit the EMC by imposing a swelling limit in dry-HT wood, preventing dry-HT wood to take-up the same amount of moisture as wet-HT wood at the same OH_{acc} content. In that case, an EMC recovery in dry-HT wood would be associated with a progressive breaking of these crosslinks, lifting the swelling limit.

Since the ratio of the slopes of the determined EMC - OH_{acc} correlations for dry-HT and wet-HT is very near 2, there is an interesting alternative explanation by taking arguments into account, that require OH_{acc}-pairs for moisture sorption in wood. In this case, the crosslinks in dry-HT wood would have an indirect role, preventing relaxation for the formation of sorption sites by combining solitary OH_{acc} from 2 thermally destructed pairs into 1 new pair. This restoration process is supposed to be fully accomplished during wet-HT, enabling wood polymer relaxation.

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SESSION FIVE

COST FP 1407

Wood Furfurylation as a way to valorise European Beech and promote Circular and Bio-Economy

Christine Gérardin[1], Aurélia Imbert[1], Prabu Satria Sejati[1], Emmanuel Fredon[1], Stéphane Dumarçay[1], Eric Masson[2], Arnaud Besserer[1], Benoit Laibe[3], Rémi Laibe[3], Hugo Sellier[3], Philippe Gérardin[1]

[1] Université de Lorraine, Inra, EA 4370 USC 1445 LERMAB, Faculté des Sciences et Technologies,
BP 70239, 54506 Vandoeuvre-lès-Nancy Cedex, France [email : christine.gerardin@univ-lorraine.fr]
[2] CRITT Bois, 27, rue Philippe Séguin, BP 91067, 88051 Epinal Cedex 9, France
[email : eric.masson@cribois.net]
[3] Métallerie du Sud Lorrain, 88500 Hymont, France [email : benoit.laibe@msl.fr]

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ABSTRACT

European beech (*Fagus sylvatica* L.) is a major tree species of European forest that is underexploited because of its low dimensional stability and weak natural durability. Its utilization in outdoor conditions involves the use of protection system like wood preservatives. However, biocides are under important scrutiny due to their potential health and environmental risks leading to increasing regulations or interdiction in most of developed countries and especially in Europe justifying the development of non-biocide alternatives for wood protection. Similarly to what has been developed with radiata pine, furfurylation might be the answer to optimize the utilization of local beech wood. Beech wood furfurylation process was studied using five different catalysts: maleic anhydride, maleic acid, citric acid, itaconic acid and tartaric acid. Optimization of the furfurylation process was investigated for different catalyst and furfuryl alcohol (FA) contents, and different duration of polymerization. The following properties were studied: weight percent gain (WPG), leachability, anti-swelling efficiency (ASE), wettability, modulus of elasticity (MOE), modulus of rupture (MOR), Brinell hardness (BH), and decay durability. Tartaric acid, never investigated up to now, was retained as catalyst to perform furfurylation due to its efficacy compared to other catalysts and its novelty. Wood modification with FA and tartaric acid as catalyst led to samples with high WPG even after leaching, improved ASE and lower wettability with water. Most of all, treatment gave a significant improvement in mechanical properties and resistance to wood decaying fungi. Based on laboratory results, a pilot scale treatment device was realized by the "Métallerie du Sud Lorrain (MSL)" an industrial partner involved in the research program on beech furfurylation (Figure 1). First results indicated that it was possible to produce large scale samples with properties similar to those measured on laboratory scale samples.

INTRODUCTION

European beech (*Fagus sylvatica* L.) is one of the most important temperate deciduous broadleaf tree species that can be found widespread across Europe and West Asia (Fang and Lechowicz 2006). Beech heartwood is not demarcated from sapwood and has a uniform white-yellowish or light brown colour. Basic density is quite high ranged from 560 to 710 kg/m^3 which makes beech wood suitable for construction material. Moisture content of fresh sawn wood is 85-95%, fibre saturation point is approximately 30-32% at room temperature. High volumetric shrinkage of beech wood ranges from 11% to 29% which leads to a high deformability following changing environmental humidity. Without any preservation treatment or modification, beech has a low natural durability when subjected to biological organisms. According to EN standard beech wood classifies as not durable against fungi, susceptible to termites attack and easily permeable to impregnation treatment.

Application with toxic or corrosive chemical may be treat to the wood to help prevent decay, improve water resistance, and reduce the effects of ultraviolet radiation (Rowell 2006). Wood modification provides an alternative by providing dimensional stability and decay resistance. Wood modification define by (Hill 2006) as the action of chemical, biological, or physical agent upon the wood material resulting in a desired property enhancement during the service life of wood. This method was proposed to replace the conventional wood preservation methods using chemical biocides. Epmeier *et al.* (2004) comparing different wood modifications properties like acetylation, modification with methylated melamine formaldehyde, furfurylation, maleoylation, succination, and thermal modification in vegetable oil, found that furfurylation was one of the most effective modification among others. Modification of wood with furfuryl alcohol (FA), known as furfurylation, has been developed in the past several decades. FA is a derivative of furfural obtained through hydrogenation process. Furfural can easily obtained from pentosans present in numerous agricultural by-products after acid hydrolysis and dehydration (Baysal *et al.* 2004). Moreover, the by-products of beech wood transformation contain high amounts of xylans, which can be used as starting material to obtain furfuryl alcohol allowing development of bio-sourced treatment based on circular economy. Polymerization of FA is generally carried out by using catalysts (organic acids, in organic acids, and dehydrating agents) and high temperature treatment (Wewerka 1968; Barr and Wallon 1971). Sejati *et al.* (2016) investigated the properties of furfurylated beech using several catalysts such as maleic anhydride, maleic acid, citric acid, itaconic acid, and tartaric acid in water solvent. The result showed that furfurylated wood catalysed by tartaric acid obtained a high performance.

Modification of wood using FA has been described to take place through different reactions (Lande *et al.* 2008): (1) homo-polymerization of FA, (2) co-polymerization and reaction with cell wall components, and (3) grafting of FA or ply(FA) to wood cell wall polymers. This statement has been confirmed by Nordstierna *et al.* (2008), who showed the formation of chemical bonds between lignin-like model molecules and poly(FA). This polymerization leads to an improvement of several physical wood properties. Esteves *et al.* (2011) reported that the furfurylation of wood reduce the equilibrium moisture content (EMC) from 17.3% to 9%. Baysal *et al.* (2004) found an improvement in anti-swelling efficiency (ASE) and decrease in water absorption (WA) of furfurylated wood. There is also an improvement in some mechanical properties of furfurylated wood (Xie *et al.* 2013) such as increase the modulus of rupture and elasticity (Lande *et al.* 2004b), and Brinell hardness (Epmeier *et al.* 2004). Meanwhile one of the drawbacks of this treatment is the decrease the impact strength (Lande *et al.* 2004b). Durability is the most crucial aspect of the wood modification. Furfurylation provide improvement of durability against wood decaying fungi (Treu *et al.* 2009; Esteves *et al.* 2011; Li *et al.* 2015; Sejati *et al.* 2016), termites (Hadi *et al.* 2005; Gascon-Garrido *et al.* 2013), marine borers (Westin *et al.* 2006), and weathering (Temiz *et al.* 2007). Even though it can have high durability against wood degradation organisms, furfurylated wood is reported to be not harmful for environment or users during and after service live, even when burned, furfurylated wood did not release more VOC or PAH than untreated wood (Vetter *et al.* 2009).

Up to now, furfurylated softwood species have been commercialized as new environmentally and durable material. However, furfurylation of beech wood has not been subjected to such developments, even if its utilization is far to be optimal due to its low natural durability and dimensional stability. Based on this finding, the aims of this paper are to describe results concerning beech furfurylation on laboratory scale and first results on pilot scale.

EXPERIMENTAL

Laboratory scale

The conditions of impregnation and polymerization, the sample preparation, the dimensional stability, the determination of MOE and MOR, the tests of durability, the statistical analysis are the same as described in Sejati *et al.* (2016).

Pilot scale

Sample preparation

Samples were prepared from beech (*Fagus sylvatica* L.) heartwood board presenting an average initial air dry density of 712 kg/m^3. Two kinds of boards measuring 1000 x 142 x 22 mm^3 and 1000 x 95 x 26 mm^3 were prepared for impregnation.

Impregnation and polymerization

Production of furfurylated beech boards was carried out in a laboratory pilot designed and built by Métallerie du Sud Lorrain (***Figure 1***).

Figure 1: pilot scale treatment device developed by MSL

Boards were vacuum-pressure impregnated using a treating solution containing 55% water, 40% furfuryl alcohol and 5% tartaric acid. The impregnated samples were air-dried at room temperature for one week. Samples were then placed again in the pilot for polymerization. The temperature was slowly increased by 0.5°C min^{-1} from ambient to 40°C and maintained at this temperature for 4 h. Then the temperature was raised to 120°C (at 0.5°C min^{-1}) for 24 h.

Anhydrous density

Anhydrous density of wood was used to evaluate the weight gain due to treatment. It was determined with samples of 20 x 20 x 20 mm^3 (five replicates) and calculated according to the following equation (Eqn. 1):

$$MV_0 = M_0/V_0 \qquad (1)$$

Wherein M_0 is the dry (0% moisture content) weight of wood sample (kg) and V_0 is the dry volume of wood sample (m^3).

Dimensional stability

Anti-swelling efficiency (ASE) was used to evaluate the dimensional stability of furfurylated wood. Tests were done with samples of 20 x 20 x 20 mm^3 (five replicates).

MOE and MOR

Global modulus of elasticity (MOE) and module of rupture (MOR) of wood were determined with samples of 400 x 20 x 20 mm^3 (five replicates) by a four point static bending test according to EN 408.

Durability

Resistance to decay was evaluated using one white rot fungus *Coriolus versicolor* and one brown rot fungus *Coniophora puteana*

RESULTS AND DISCUSSION

Laboratory scale

Table 1 describes the effect of different FA concentration and tartaric acid concentration on the effectiveness of polymerization of FA into the wood as well as some wood properties like anti-swelling efficiency (ASE), leachability, MOE, and MOR.

WPG and Leachability

Weight percent gains (WPG) are directly connected to the density increase observe with the increase of FA content in the impregnation solution. The highest WPG obtained by 50% of FA, 20% of tartaric acid and 30% water treated wood (72.2%). High level of FA content (90% and 95%) resulted lower WPG than we expected (49.6% and 37.9%). This result indicated that the optimum condition to obtain higher WPG of furfurylated beech wood was 50% of FA in water as solvent. Higher level of FA will not increase WPG significantly. Leaching tests were used to evaluate the fixation of FA in wood during service. Leachability of polymer form in wood expressed as weight loss due and varies between 1.2% and 5.3%.

Dimensional Stability

Anti-swelling efficiency (ASE) of furfurylated wood ranged between 21.3% and 67.0%. In Table 1 we can see that there is a correlation between ASE and quantity of FA used for the treatment that represent WPG. Our result are consistent with those reported by Baysal *et al.* (2004) indicating that higher ASE value can be reached for higher WPG, bringing wood structure bulking and increasing its dimensional stability. Highest value of ASE obtained respectively by treatment of FA 90%, 5% TAc, 5%, water 5% (67%), followed by treatment of FA 50% with water as solvent (66.4%). More surprisingly, ASE values of the highest WPG (treatment FA 50%, TAc 20%, water 30%) and higher utilization FA (treatment FA 95%, TAc 5%) only reach 59.8% and 59.8% respectively. According to these results, it can be concluded that FA 50% seems a good compromise in term of cost due to utilization of FA to obtain high value of ASE. There is a limit where further increase in WPG does not lead to a significant higher dimensional stability (Lande *et al.* 2004b). Improvement of dimensional stability in furfurylated wood can be explained by the polymerization inside the wood structure, in the lumen and in the cell walls, that prevents the water molecules to reach the wood polysaccharides, reducing thus equilibrium moisture content and increasing dimensional stability and durability (Esteves *et al.* 2011). Reticulation reaction between FA polymer, catalyst and wood components may also explain the lower susceptibility of the material to bulking and its higher dimensional stability.

Table 1. Weight percent gain (WPG), anti-swelling efficiency (ASE), leaching, MOE, MOR, density and durability of beech laboratory scale wood sample subjected to different treatments of furfuryl alcohol (FA) in water

Treatment	WPG (%)	Leaching (%)	ASE (%)	MOE (N/mm^2)	MOR (N/mm^2)	Density (kg/m^3)	Weight Loss (%)	Durability class (EN 350-1)
FA 25%, TAc 5%, Water 70%	25.5±1.00	4.2±1.6	44.7±2.7	12422±909 B	124±11 B	741±33 B	8.9±2.6	1
FA 30%, TAc 5%, Water 65%	26.1±0.01	2.0±0.2	43.6±0.0	13149±156 AB	122±4 AB	784±1 C	5.1±0.1	1
FA 40%, TAc 5%, Water 55%	34.1±0.06	1.9±0.2	48.5±4.0	13308±390 B	106±3 A	871±1 D	3.1±0.2	1
FA 50%, TAc 5%, Water 45%	38.5±3.20	5.3±0.8	66.4±0.8	12290±658 B A	109±7 A AB	758±14 B A	2.7±0.6	2
FA 50%, TAc 20%, Water 30%	72.2±0.03	3.1±1.4	59.8±4.4	10986±184 A	86±3 A	972±10 D	2.4±0.1	1
FA 90%, TAc 5%, Water 5%	49.6±0.54	1.6±0.3	67.0±2.0	12355±482 B	104±7 B	820±21 B	2.4±0.2	1
FA 95%, TAc 5%	37.9±1.08	1.2±0.1	59.8±2.7	14677±320 C A	140±3 D C	847±11 C A	3.3±0.1	1
Untreated				10301±569 A/A/A/A	117±5 A/AB/AB/C	624±2 A/A/A/A	39.1±9.2	5

Mechanical Properties

The MOE of furfurylated beech wood varies between 10986 N/mm^2 and 14677 N/mm^2, meanwhile untreated beech wood is 10301 N/mm^2. The highest value of MOE obtained by low level of furfurylation used 40% FA, 5% TAc, and 45% water, that show 29% increase of MOE. High level of furfurylation used 50% FA resulted similar increase of MOE about 19% in ater. The lowest MOE obtained by the highest WPG treatment 50% FA, TAc 20%, and 30% water even there is still a little increase of MOE than untreated wood. MOR of furfurylated beech wood has a similar tendency as the MOE value. The MOR varies between 86 N/mm^2 (treatment 50% FA, TAc 20%, and 30% water) and 140 N/mm^2 (treatment 95% FA, 5% TAc). Higher MOR value obtained by treatment 95% FA and 5% TAc (140 N/mm^2) and treatment 50% FA, 5% TAc, and 45% water (127 N/mm^2). MOE of each treatment agreed with its density value. Generally all furfurylation treatment of beech wood was improved MOE value, nevertheless there are some treatment reduce MOR value. This result is confirmed by Sejati *et al.* (2016) which reported that furfurylation on beech wood lead an increasing of MOE, explained by Lande *et al.* (2004b) that the permanent bulking and grafting of FA polymer to the cell structure affect the stiffness, strength and brittleness of the wood. However, Pfriem *et al.* (2012) found reduction of MOE in furfurylated beech wood catalyzed by maleic anhydride, while the other research concluded that MOE was not significantly changed by furfurylation (Epmeier *et al.* 2004; Esteves *et al.* 2011; Li *et al.* 2015).

Durability

Durability of furfurylated wood samples in terms of resistance to the white rot decay fungus *Coriolus versicolor* was measured before and after leaching to make sure the effectiveness of the polymerization process to protect wood after accelerated leaching test. Weight loss due to decay fungi attack of furfurylated beech wood varies between 2.4% and 14% or durability class

1 (very durable) to 2 (durable) according to EN 350-1, meanwhile weight loss of untreated beech wood was 39.1% or durability class 5 (not durable). There is no significant difference of durability between measurement before or after leaching. It can be shown from the same durability class of both weight loss. According to our results, FA concentration to achieve efficient protection with weight loss of wood sample inferior 6% is comprised between 30% and 50% for the treatment in water. Meanwhile, different content of FA and TAc at high level of furfurylation did not affect significantly decay durability than treatment of 50% FA. Treu *et al.* (2009) reported weight loss of 0.7% for beech wood furfurylated with a WPG of 29.6%, while untreated beech presented weight losses of 29.5%. Furfurylation gives high protection against biodegradation (fungi, marine borers and termites) at moderate and high level of modification. The penetration of resin into the wood cell wall or even cross-linkage reaction between FA and wood cell wall components changes the chemical nature of the cell wall, thus making it unattractive to decay fungi showed by a clear decrease in mass loss due to fungal attack (Lande *et al.* 2004b; Lande *et al.* 2008; Esteves *et al.* 2011; Li *et al.* 2015). Nevertheless, Pilgard and Alfredsen (2009) suggest that wood modification results in physical blocking of the entrance of decay and the reduction of equilibrium moisture content. It is more difficult for fungi to get the moisture required for decay.

Pilot scale

Pilot scale polymerization of furfuryl alcohol into wood resulted in a significant improvement of anhydrous density and dimensional stability (Table 2).
ASE ranges between 47 and 50%. Furfurylation increases the MOE in bending of beech wood boards by 24% to 41%. After treatment, the modulus of rupture decreases for one sample and remains unchanged for the others.

Table 2. Density, anti-swelling efficiency (ASE), MOE, MOR, and durability of beech pilot scale wood samples subjected to treatment of furfuryl alcohol (FA) in water

Sample	Density (kg/m^3)	ASE (%)	MOE (N/mm^2)	MOR (N/mm^2)	Weight Loss (%)		Durability Class
					CV	CP	
B-I	808 ± 4	48 ± 3	18293 ± 614	78 ± 11	1.5 ± 0.4	1.5 ± 0.6	1
B-II	881 ± 10	50 ± 2	16447 ± 1033	91 ± 15			
B-III	807 ± 3	47 ± 5	15425 ± 2118	91 ± 17			
B-I untreated	655 ± 12	-	12968 ± 511	110 ± 8	18.8 ± 7.6	23.5 ± 10.1	5
B-II untreated	693 ± 3	-	13246 ± 815	100 ± 5			
B-III untreated	660 ± 9	-	11483 ± 1010	89 ± 7			

The resistance of the furfurylated beech wood boards to the white rot decay fungus *Coriolus versicolor* and the brown rot fungus *Coniophora puteana* are also presented in Table 2. According to EN 350-1, these furfurylated samples can be categorized in durability class 1.

CONCLUSION

Disadvantages of natural beech wood can be improved by furfurylation process. From our results, furfurylation of beech wood using 50% FA and water as solvent lead higher WPG. Higher level of FA will not increase WPG significantly. Similarly to WPG, optimum dimensional stability of furfurylated wood is obtained by the same treatment. All furfurylation treatments lead to an improvement of MOE. High level of furfurylation can slightly reduce MOR. Furfurylated wood obtained high protection against fungal attack. The conditions of furfurylation were adapted to pilot scale and regarding all of properties observed, furfurylated wood at 40% FA and 5% TAc in water seems to be an optimum condition to reach maximum improvement of beech wood properties at the laboratory scale as well as at the pilot scale.

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Dynamic Mechanical Thermal Analysis of Wood Modified with Bio-Polyesters

Charlotte Grosse[1,2], Morwenna Spear[3], Simon Curling[3], Marion Noël[1], Lauri Rautkari[4], Tuuli Uimonen[4] and Philippe Gérardin[2]

[1]Bern University of Applied Sciences; Department Wood, Architecture and Civil Engineering, Solothurnstrasse 102, 2500 Biel, Switzerland [email: charlotte.grosse@bfh.ch]
[2]LERMaB, EA 4370, Université de Lorraine, Faculté des Sciences et Technologies, Vandoeuvre-lès-Nancy, France [email: philippe.gerardin@univ-lorraine.fr]
[3]BioComposites Centre, Bangor University, Bangor, Gwynedd LL57 2UW, UK
[email: m.j.spear@bangor.ac.uk; s.curling@bangor.ac.uk]
[4]Aalto University, Department of Bioproducts and Biosystems, Vuorimiehentie 1, 02150 Espoo, Finland [email: lauri.rautkari@aalto.fi; tuuli.uimonen@aalto.fi]

Keywords: beech, bio-polyester, hydrothermal treatment, impregnation, lactic acid, polybutylene succinate, wood modification

ABSTRACT

Chemical modification of wood with bio-polyesters, namely polylactic acid (PLA) and polybutylene succinate (PBS), has recently been reported (Noël *et al.* 2015, Grosse *et al.* 2017a). Both oligomeric treatments (OBS and OLA) confer interesting properties to wood for outdoor applications. They are based on the impregnation of oligomers in oven-dried beech wood (*Fagus sylvatica* L.), followed by a curing step at 100 or 120°C for OBS or 160°C for OLA. Unlike treatment with OLA, the dry curing conditions did not allow any penetration of OBS in wood cell walls, thus no gain in anti-swelling efficiency (ASE) was seen. Humid treatment conditions were observed to allow a partial diffusion of OBS in cell walls, most likely because of water acting as swelling agent. Hydro-thermal treatment (HTT) was carried out at several temperatures, relative humidities and durations, to find optimal conditions of OBS diffusion in the wood structure. Treatment conferred ASE of 60% to 70%, with a good correlation to OBS diffusion. (Grosse *et al*. 2017b). In this study, dynamic mechanical thermal analysis (DMTA) under varying humidity was carried on for understanding OBS/OLA interactions with wood polymers. First, temperature scans were performed from -150°C to 150°C at a heating rate of 5 °C/min and for a frequency of 1, 10 and 100 Hz. Glass transitions of wood components and oligomers appeared in the tan δ response of the modified wood. In a second set of experiments the relative humidity in the chamber was set at 35% and the temperature changes were manually performed when the conditions in the chamber were stable. Wood impregnated with OBS but not hydrothermally-treated has the same behaviour as untreated wood, indicating few interactions between the polymer and the cell walls. This is well correlated with the low diffusion of OBS into wood structure. In the case of hydrothermally-treated samples the same global behaviour can be observed. In the case of OLA treated wood, the stiffness of the material decreases more rapidly with the temperature, in comparison with the OBS treated wood. Oligomers of lactic acid, more hydrophilic and smaller than the PBS ones, are more likely diffusing then interacting with the cell walls polymers.

INTRODUCTION

As a renewable material, wood has many advantageous properties such as workability, mechanical strength, sustainability and pleasant aesthetic features. However, wood is sensitive to its environment, especially regarding moisture. Due to its chemical composition, the dimensional stability against humidity and biological resistance of wood are limited. Chemical modification of wood with polybutylene succinate (PBS) has been reported to confer interesting properties to wood for outdoor applications (Noël *et al.* 2015a, 2015b, Vitkeviciute *et al.* 2014). This treatment was based on the hot impregnation (90°C) of PBS in oven-dried beech wood (*Fagus sylvatica* L.), followed by a curing step at 100/120°C for 6h/96h. The dry treatment conditions did not allow any penetration of the oligomers in wood cell walls, thus any anti-swelling efficiency (ASE). The mechanical properties were not influenced either. However, the PBS lumen-filling led to a substantial decrease in wood hygroscopicity. Moreover, a good retention of oligomers into the wood lumens was observed, with ca. 80% retention rate of the impregnated polymers in wood during water leaching. Humid treatment conditions were observed to allow a partial diffusion of the oligomers into the cell walls, most likely because of water acting as swelling agent inducing partial penetration of oligomers in the cell wall. Humid treatment conferred anti-swelling efficiency (ASE) of 60% to 70%, with a good correlation to PBS diffusion. This phenomenon is not yet fully understood. For that reason, the dynamic mechanical thermal analysis (DMTA) under varying humidity is expected to help the understanding. Hydro-thermal treatment (HTT) was carried out at several temperatures, relative humidity and duration, in order to find optimal conditions of PBS diffusion into the wood structure. Most effective HTT to carry out for eventual up-scaling is to be determined: low temperature for long time, or short time at high temperature. The question of wood components degradation might be decisive. DMTA under varying humidity is expected to help the selection of the best option through analyse of the influence of treatment parameters (temperature, relative humidity and duration) on wood/oligomers interactions.

EXPERIMENTAL

Samples preparation

Samples were prepared as described by Noël *et al*. (2015b). Oven-dried wood samples were immersed in liquid oligomers, OBS, OLA L and OLA S respectively, at 90°C, 60°C and 20°C respectively. Containers were then placed in a vacuum oven under reduced pressure (150 mbar) for 20 to 30 min, then atmospheric pressure over 20 to 30 min. Impregnated samples were then wiped.

Weight uptake (WUi) and swelling (Si) after impregnation have been calculated as follows:

$$\mathrm{WU_i}\ (\%) = \frac{\mathrm{w_i} - \mathrm{w_{u,d}}}{\mathrm{w_{u,d}}} \times 100 \qquad (1)$$

$$\mathrm{S_i}\ (\%) = \frac{\mathrm{V_i} - \mathrm{V_{u,d}}}{\mathrm{V_{u,d}}} \times 100 \qquad (2)$$

where $\mathrm{w_i}$ and $\mathrm{V_i}$ stand for the impregnated sample weight and volume respectively and $\mathrm{w_{u,d}}$ and $\mathrm{V_{u,d}}$ for the sample untreated anhydrous weight and volume.

For the OBS-treated samples, the following HTT was carried out in a pressurized reactor at 100% relative humidity (RH) and different temperatures for different durations. For all samples, a final thermal post-treatment (PT) was carried out to dry the treated samples and was expected to partially cure and fix the oligomers in wood. Table 1 summarises the treatments conditions.

Weight uptake (WUt) and swelling (St) after treatment were calculated as follows:

$$\mathrm{WU_t}\ (\%) = \frac{\mathrm{w_{t,d}} - \mathrm{w_{u,d}}}{\mathrm{w_{u,d}}} \times 100 \qquad (3)$$

$$\mathrm{S_t}\ (\%) = \frac{\mathrm{V_{t,d}} - \mathrm{V_{u,d}}}{\mathrm{V_{u,d}}} \times 100 \qquad (4)$$

where $\mathrm{w_{t,d}}$ and $\mathrm{V_{t,d}}$, and $\mathrm{w_{u,d}}$ and $\mathrm{V_{u,d}}$ respectively stand for treated and untreated samples anhydrous weight and volume respectively. All samples were then stabilised at 35% RH.

Table 1: description of treatments conditions

Sample	Impregnation product	Hygro-thermal treatment			Post treatment	
		Temperature [°C]	RH [%]	Duration [h]	Temperature [°C]	Duration [h]
PBS A	PBS	100	100	2	103	72
PBS B					120	72
PBS C		130	100	0.5	103	72
PBS D					120	72
PBS E		160	100	0.5	103	72
PBS F					120	72
PBS G		-	-	-	103	72
PBS H		-	-	-	120	72
OLA S	Short OLA	-	-	-	160	48
OLA L	Long OLA	-	-	-	160	48
REF	None	-	-	-	-	-

Dynamic mechanical analysis

First, the dynamic mechanical thermal analysis (DMTA) has been carried out on a Triton TTDMA. Temperature scans were performed from -150°C to 150°C at a heating rate of 5 °C/min and for a frequency of 1, 10 and 100 Hz.

A second DMA analysis has been then carried out using a humidity generator connected to the Triton TTDMA, to allow a temperature ramp while controlling the RH in the chamber. Samples of dimensions 50×10×4mm (L×RT×TR) were used in both sets of experiments. RH was set at 35% and the temperature changes were manually performed when the conditions in the chamber were stable. Once the temperature and RH were stable, the average of five values of the stabilised storage modulus was calculated. Only relative storage modulus values and tan delta for 1Hz are reported.

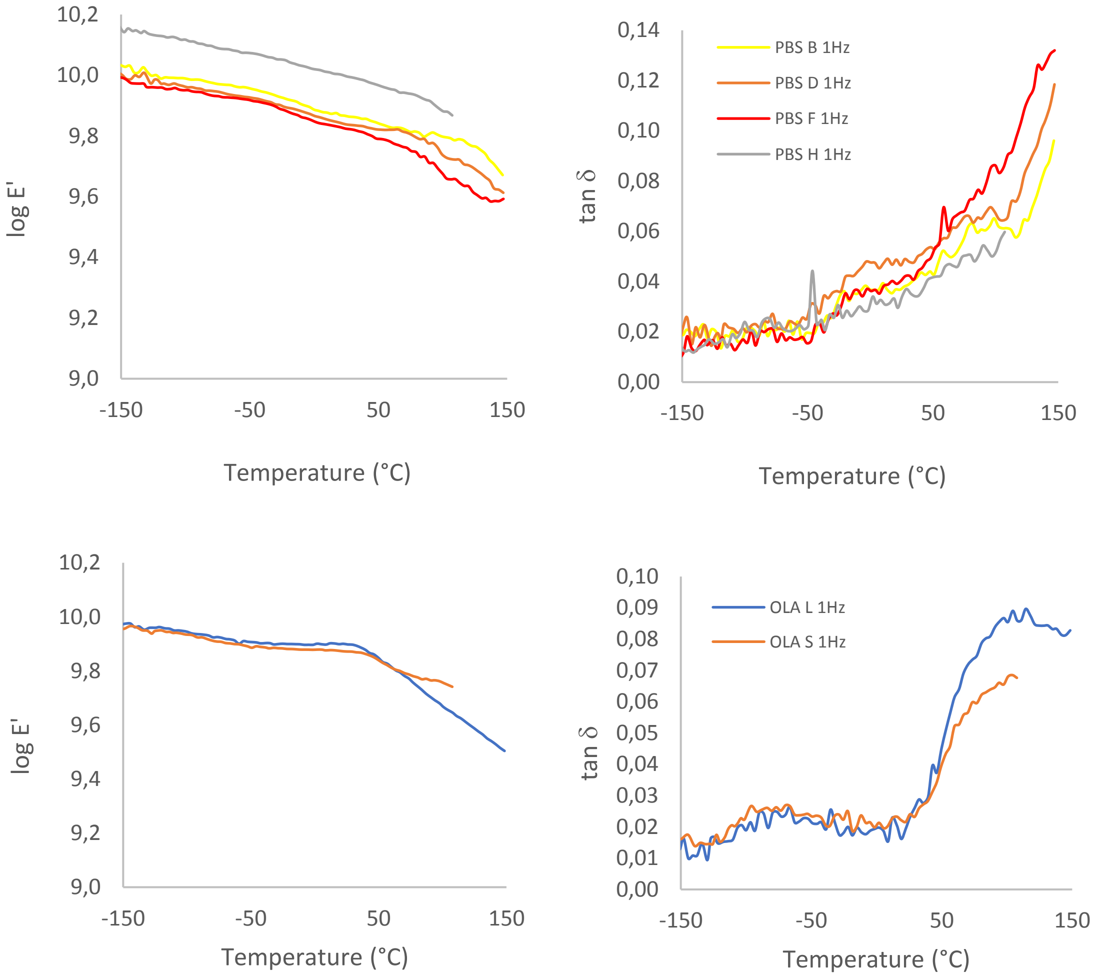
RESULTS AND DISCUSSION

Dynamic mechanical thermal analysis (DMTA)

Table 2 summarises samples weight and volumetric variations during treatment. After impregnation, both polymers mostly remain in the cell lumens according to the low S_i. With heating, there is a product migration into the wood structure. S_t is most likely due to product diffusion in the cell walls. For PBS, diffusion is more effective with HTT than with only PT and for OLA, a PT carried out at 160°C is sufficient.

Table 2: Samples weight variations (WUi and WUt) and volumetric variations (Si and St) after impregnation and after treatment (only the data of the one sample used for DMTA are presented).

	WUi [%]	WUt [%]	Si [%]	St [%]
PBS B	86.9	77.5	0.5	15.1
PBS D	88.7	80.2	1.8	13.7
PBS F	82.4	66.1	2.6	12.8
PBS H	79.1	75.1	1.8	7.6
OLA S	62.7	29.9	0.4	12.1
OLA L	81.8	51.1	-0.5	16.3



(a) (b)

Figure 1: Effect of polymers on the dynamic mechanical response (a) log E' and (b) tan δ for a frequency of 1Hz.

Wood DMTA has been widely studied. The tan δ response of untreated wood usually shows a low temperature transition (β) at between -90 and -110 °C, and a broad transition (α1) centred around 80 to 100°C with a shoulder (α2) between 10 and 60°C (Kelley *et al*. 1987). Glass transition temperature (T_g) of PBS and PLA respectively is around -45 to -50 °C and around 40 to 60°C respectively. As oligomers present in the modified wood are smaller than industrial polymers, those transitions might appear in the lower range of temperature in the tan δ response of the modified wood (Figure 1).

For PBS treated wood, the tan δ response is very similar to untreated wood. However, the β transition is not clear and α1 transition might have been shifted to slightly higher temperature, showing a reduced amount of small molecules in wood structure and reduced mobility of cell walls components. A transition around -50 °C appears in the tan δ response of PBS H but not in the others. It might just be a measurement error or it can be the T_g of PBS from the lumens as it is the only variant not submitted to hydrothermal treatment. For OLA treated wood, the β transition is visible around -80 °C and α1 is broader than for untreated wood. α1 transition is most likely due to both wood and OLA as the PLA T_g is around 40 to 60 °C.

Effect of PBS on the dynamic mechanical response at 35% RH

Table 3 summarise samples weight and volumetric variation during treatment. First, one sample for each variant was run on the DMA after stabilisation in a desiccator at 35% RH. At this RH, treated samples were very dry as they all had an EMC below 2%. Figure 2 and Figure 3 show the relative storage modulus (E’) and tan δ response for this first batch of samples. The reference sample (REF) relative E’ is slightly increasing (about 5%) with the temperature from 20 to 30 °C and is then decreasing back to its original value at 20°C. Wood impregnated with PBS but not hydrothermo-treated (PBS G) has the same behaviour indicating few interactions between the polymer and the cell walls. This is well correlated with the low diffusion of PBS into wood structure (S_t = 3.1%). Impregnation followed by heat treatment at 120°C allows to double the wood swelling after treatment (PBS H). Relative E’ is increasing with the temperature but seems to stabilise instead of decrease. In the case of samples impregnated with PBS and then treated with hydrothermal treatment and post-treatment (PBS A, B, E, and F), the same behaviour can be observed. Relative E’ is decreasing with temperature. However, some variants ran a second time, with another sample, showed opposite behaviour, like PBS A (Figure 4). Information provided is not fully understood yet, but reproducibility of the experiment is uncertain. Thus, several replicates are currently on going to validate the results and understand the reasons of such variability.

Table 3: Samples weight variations (WUi and WUt) and volumetric variations (Si and St) after impregnation and after treatment (only the data of the one sample used for DMTA are presented).

	WUi [%]	**WUt [%]**	**Si [%]**	**St [%]**
PBS A3	80.7	74.6	-0.4	14.9
PBS A2	90.5	84.6	0.1	15.8
PBS B	85.8	78.6	1.2	15.4
PBS E	86.8	72.2	2.4	13.9
PBS F	86.2	69.1	4.4	13.1
PBS G	77.9	75.8	0.3	3.1
PBS H	80.1	76.6	1.0	7.4
REF	-	-	-	-

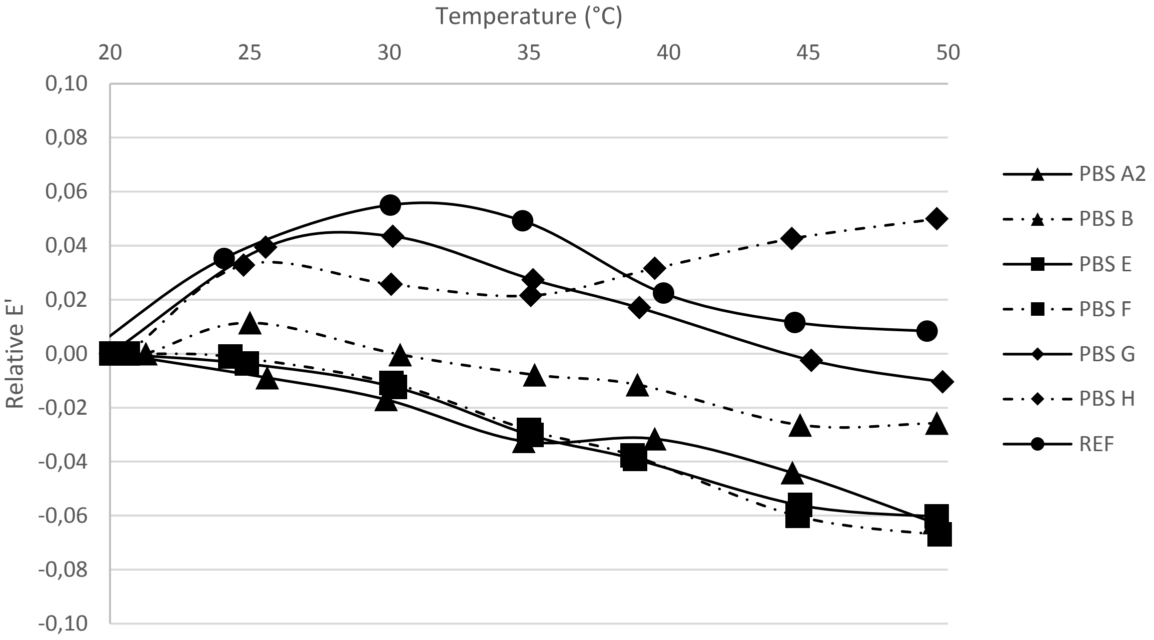


Figure 2: Effect of PBS on the dynamic mechanical response regarding relative E' for a frequency of 1Hz.

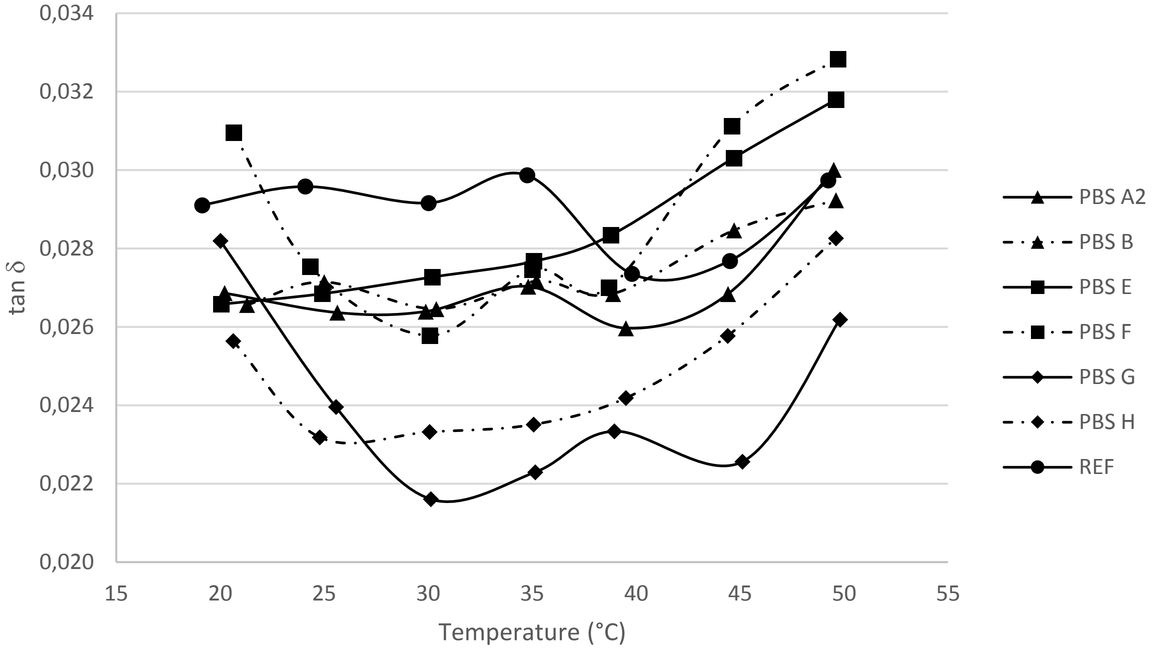


Figure 3: Effect of PBS on the dynamic mechanical response regarding tan δ for a frequency of 1Hz.

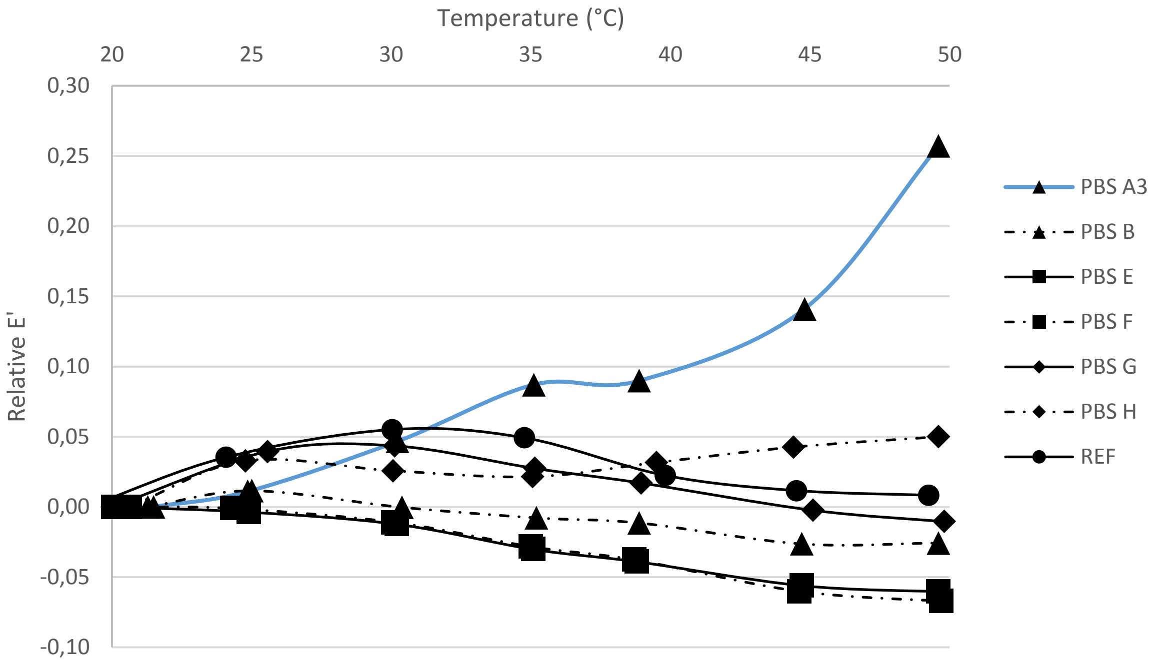
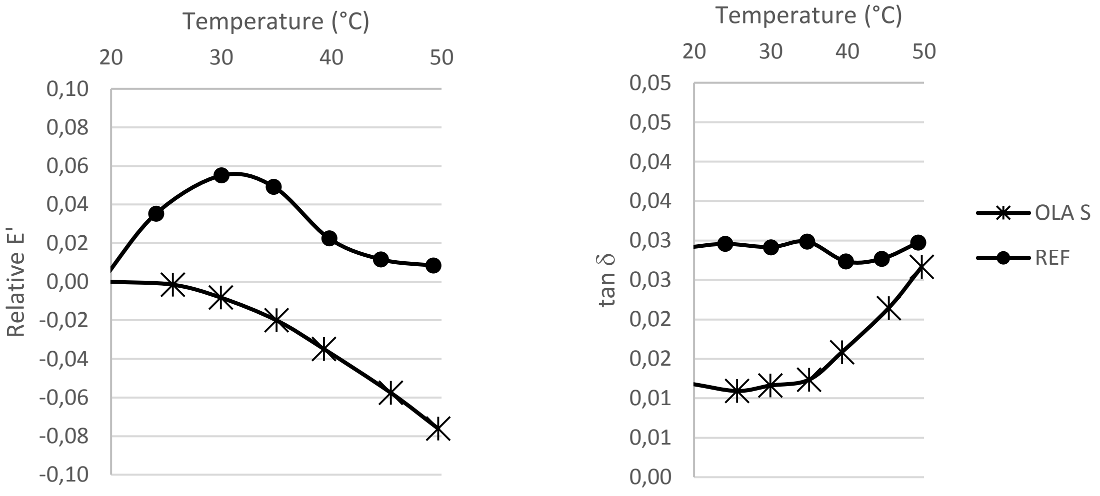


Figure 4: Effect of PBS on the dynamic mechanical response regarding relative E' for a frequency of 1Hz.

Effect of OLA on the dynamic mechanical response at 35% RH

In the case of OLA treated wood, the stiffness of the material decreases more rapidly with the temperature in comparison with the PBS treated wood. Oligomers of lactic acid, more hydrophilic and smaller than the PBS ones, are more likely diffusing then interacting with the cell walls polymers.



(a)

(b)

Figure 5: Effect of OLA on the dynamic mechanical response regarding (a) relative E' and (b) tan δ for a frequency of 1Hz.

CONCLUSIONS

As conclusion, the DMA provided interesting pre-results and revealed to be a possible way to investigate the influence of hydrothermal treatment and post-treatment conditions on the mechanical properties, as well as on the interaction of wood with the polymer. However, more experiments are still on going to reinforce the analyse and the results.

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Perception and evaluation of modified wood

Dean Lipovac, Michael D. Burnard[2] and Andreja Kutnar[3]

[1]InnoRenew CoE, Livade 6, 6310 Izola, Slovenia [email: dean.lipovac@innorenew.eu]
[2]InnoRenew CoE, Livade 6, 6310 Izola, Slovenia; University of Primorska, Andrej Marušič Institute, Muzejski trg 2, 6000 Koper, Slovenia [email: mike.burnard@innorenew.eu]
[3]InnoRenew CoE, Livade 6, 6310 Izola, Slovenia; University of Primorska, Andrej Marušič Institute, Muzejski trg 2, 6000 Koper, Slovenia; Faculty of Mathematics, Natural Science, and Information Technology [email: andreja.kutnar@innorenew.eu]

Keywords: evaluation, perception, preference, tactile, visual, wood modification

ABSTRACT

Wood modification processes improve many characteristics of wood that are appreciated among building professionals. The same modification processes also change characteristics of wood that are important to laypeople, such as wood's visual (e.g., colour) and tactile (e.g., roughness) properties. Since these properties are crucial in people's perception and evaluation of materials, it is necessary to study how people perceive and evaluate modified wood. To assess human perception and evaluation of modified wood compared to untreated wood and steel, we prepared six cylindrical handrail samples. They were from unmodified spruce, unmodified pine, acetylated radiata pine, thermally modified spruce, thermally modified pine or stainless steel. 50 participants aged 65 or above rated all samples in random order on a 9-item semantic differential scale, which consisted of sensory (e.g., rough-smooth) and evaluative (e.g., like-dislike) pairs of descriptors. The study consisted of a tactile only task, visual-tactile task, and ranking task. The results indicate that modified wood is perceived and evaluated similarly to untreated wood both in the tactile and the tactile-visual task, while the stainless steel was perceived as considerably different than all types of wood. Ratings of the same handrails between the tactile and the tactile-visual task were similar, which suggests that touch has an important role in perception and evaluation of materials. The two highest ranked handrail samples were both manufactured from modified wood. Taken together, the findings indicate that modified wood possesses tactile and visual features that are comparable to untreated wood and are in general liked among older adults. These findings encourage the use of wood in indoor environments.

INTRODUCTION

Wood modification processes, such as thermal modification, can enhance several characteristics of wood including dimensional stability, durability against decay, and increased resistance against fungi and insects (Sandberg *et al*. 2017). Since these enhancements are useful in the construction field, it is not surprising they are valued among building professionals. However, modified wood does not obtain only transformed mechanical, biochemical and thermal properties, but also qualities that are available directly to our senses, such as colour, dryness or roughness (Bakar *et al*. 2013, Esteves and Pereira 2009). The combination of these basic sensory properties plays an important role in the general evaluation of materials by laypeople, where characteristics such as pleasantness, price, naturalness, and others are assessed (Fujisaki *et al*. 2015, Kidoma *et al*. 2017).

Better evaluated materials are not only more attractive to consumers, but can also provide direct health benefits. Based on the tactile information, wood is evaluated more favourably than marble, tile, and steel. In addition, subjects touching wood experience improved mood and decreased physiological arousal when compared with the tactile experience of other common materials (Ikei *et al*. 2017b). Even when the differences between materials do not seem significant, resulting perceptions and evaluations are nonetheless changed. Different coatings on the same material are enough to produce distinct evaluations and physiological reactions (Bhatta *et al*. 2017, Ikei *et al*. 2017a). For instance, subjects touching uncoated wood rated it as more natural than wood with either oil, vitreous, urethane or mirror finish. A mirror-finished wood sample was in general rated as the least favoured and was the only material in the study to induce an undesirable increase in physiological arousal (Ikei *et al*. 2017a). Along with the tactile qualities, visual characteristics of materials also play an important role in the evaluation of materials. For example, brighter samples of wood are perceived as more new and relaxing, but less interesting than darker materials (Fujisaki *et al*. 2015). Additionally, visual exposure to a wood panel induces improved mood and a decrease in physiological arousal, while watching a steel panel produces the opposite effect (Sakuragawa *et al*. 2005).

Taken together, current findings suggest that physical qualities of materials significantly influence human perception and evaluation, which is, in turn, associated with changes in mood and physiological states. Therefore, to be able to choose and develop appealing and healthy materials, it is important to assess how people perceive and evaluate them. Since modified wood exhibits several advantages over untreated wood, it seems reasonable to predict that its usage will keep increasing over time. However, it is not known how people perceive and evaluate wood that undergoes modification processes. Investigating this will lead us towards creating new materials that are not only valuable in construction, but also attractive and healthy for everyday users. This is especially important in the indoor environments occupied by aging individuals, whose physical abilities may be limited, which often results in a need for supportive/assistive elements of the environment. One of the features that can significantly contribute to the physical mobility of older adults is the availability and suitability of support rails and handrails.

Our study assessed how people perceive and evaluate handrails manufactured from modified wood compared to handrails produced from untreated wood and stainless steel based on touch alone in addition to touch and vision combined. Furthermore, we examined which sensory tactile and visual characteristics (e.g., roughness, lightness) are associated with general evaluation and preference of the materials. Finally, we investigated perception and evaluation of the same materials between the tactile and the tactile-visual task.

EXPERIMENTAL

Handrail samples

To investigate perception and evaluation of modified wood we prepared six cylindrical handrail samples. One sample was produced from stainless steel, while the remaining five were manufactured from either untreated or treated spruce or pine. Specifically, we included unmodified spruce, unmodified pine, acetylated radiata pine, thermally modified spruce, and thermally modified pine. The thermal modification was done with the commercial ThermoD process at 212°C and superheated steam at Heatwood (Hudiksvall, Sweden). Handrail samples measured 42mm in diameter and were 30cm long. Each sample was mounted on a wooden base covered with white foil measuring approximately 30 x 15 x 5 cm. All six samples are presented below (Figure 1).

Figure 1: Handrail samples (from left to right: unmodified spruce, unmodified pine, acetylated radiata pine, thermally modified pine, thermally modified spruce, stainless steel)

Procedure

The study consisted of three parts. In the first part, participants separately rated each handrail sample by touch only – they were instructed to keep their eyes closed (tactile task). Samples were presented to them in random order. For each handrail, subjects provided a verbal answer for each item on a semantic differential scale that was read to them. In the second part of the study, participants rated the samples again in the same order, except they were able to both touch and see the handrails (tactile-visual task). In the third part, the participants were presented all the samples at once to simultaneously see and touch. They were asked to rank them from the most to least preferred by placing cards numbered from one (preferred) to six (least preferred).

Semantic differential scale

The scale was partly based on the descriptors of the Tactile Perception Task (TPT; Guest *et al*. 2011) that were translated to Slovene. TPT assesses both sensory (e.g., dry) and evaluative (e.g., pleasant) aspects of touch. Some descriptors in the TPT were excluded since they were judged as inappropriate for the assessment of chosen materials (e.g., sensual). We also excluded descriptors that were similar in meaning to already adopted descriptors (e.g., we excluded “enjoyable” due to already including “pleasant”). To each descriptor that remained, we added a polar opposite descriptor and ended up with five word pairs (e.g., pleasant – unpleasant). In addition to the descriptors adopted from the TPT, we included one pair of tactile descriptors (soft – hard) and two pairs of visual descriptors (dark – light, shiny – matte) that were used in other studies (e.g., Fujisaki *et al*. 2015) and deemed relevant. Furthermore, we added three relevant pairs of evaluative descriptors (unusual – usual, natural – artificial, cheap – expensive). In total, the scale consisted of 11 word pairs. Two of these (dark – light, shiny – matte) were used only in the second part of the study (tactile-visual task). Six of 11 pairs of descriptors measured basic sensory properties (rough – smooth, warm – cold, dry – damp, hard – soft, dark – light, shiny – matte) while the remaining five measured the evaluation of materials (unusual – usual, natural – artificial, cheap – expensive, pleasant – unpleasant, dislike – like). For each word pair, subjects selected their answer from a 5-point scale that consisted of the adverbs “considerably”, “somewhat”, “in the middle”, “somewhat” and “considerably”. For example, on a “rough – smooth” pair, subjects could indicate that the rated sample is “considerably rough”, “somewhat rough”, “in the middle”, “somewhat smooth” or “considerably smooth”. The complete scale is presented below (Table 1).

Table 1: Semantic differential scale

	Considerably	Somewhat	In the middle	Somewhat	Considerably	
Rough	-2	-1	0	1	2	Smooth
Warm	-2	-1	0	1	2	Cold
Dry	-2	-1	0	1	2	Damp
Soft	-2	-1	0	1	2	Hard
Unusual	-2	-1	0	1	2	Usual
Natural	-2	-1	0	1	2	Artificial
Cheap	-2	-1	0	1	2	Expensive
Pleasant	-2	-1	0	1	2	Unpleasant
Dark[a]	-2	-1	0	1	2	Light[a]
Shiny[a]	-2	-1	0	1	2	Matte[a]
Dislike	-2	-1	0	1	2	Like

[a] *Only used in the tactile-visual task*

Participants

The participants were invited to the study and tested in an activity centre for older adults located in Koper, Slovenia. Invited subjects had to be at least 65 years old and possess no health impairments that would interfere with the study protocol (e.g., heavily impaired vision). Subjects were not given any incentives for participation. Approximately 15% of the approached subjects chose to participate in the study. Before beginning testing, each subject signed an informed consent document to participate in the study. Altogether, 50 persons over the age of 65 (M = 72.02, SD = 6.36) took part in the study, of those 27 (54%) were women. Participants were tested in a room with no natural lighting – the amount of indoor light was thus fixed and similar for all participants. The duration of the test was approximately 30 minutes.

RESULTS AND DISCUSSION

We separately present results from the tactile, tactile-visual, and ranking task. In addition, we report correlations between descriptors within each – tactile and tactile-visual - task. Finally, we present correlations among the same descriptors between the tactile and tactile-visual task.

Mean scores and standard deviations for all pairs of descriptors and handrail samples in the tactile task are presented below (Table 2). The scores range from -2 (e.g., considerably rough) to 2 (e.g., considerably smooth). The scores of perceived warmness, dryness and softness are similar among all wooden handrails – they were perceived as somewhat warm, dry, and soft. Handrails created from modified wood were perceived as somewhat smooth, while the untreated handrails were perceived as slightly rougher. Wooden handrails were all perceived as neither cheap or expensive and somewhat/considerably usual, natural, pleasant and liked. Steel was on average perceived as smoother, colder, damper, and harder than wood (Table 2). In addition, it was evaluated as less natural, pleasant and liked, as well as slightly more expensive and unusual.

Table 2: Tactile task scores – M(SD)

	Spruce	Pine	A.Pine	T.M.Pine	T.M.Spruce	Steel
Rough (-2) – Smooth (2)	-0.66	-0.08	1.4	0.54	1.06	1.78
	(0.98)	(0.92)	(0.81)	(1.01)	(1.04)	(0.62)
Warm (-2) – Cold (2)	-0.76	-0.68	-0.74	-0.94	-1.06	1.46
	(0.87)	(0.98)	(0.88)	(0.96)	(0.87)	(0.71)
Dry (-2) – Damp (2)	-1.24	-1.36	-1.44	-1.36	-1.48	-0.56
	(0.96)	(0.80)	(0.84)	(0.88)	(0.81)	(1.51)
Soft (-2) – Hard (2)	1.00	0.88	1.08	0.76	0.96	1.8
	(1.07)	(1.12)	(1.24)	(1.36)	(1.23)	(0.73)

	Spruce	Pine	A.Pine	T.M.Pine	T.M.Spruce	Steel
Unusual (-2) – Usual (2)	1.30	1.18	1.5	1.46	1.22	0.8
	(1.34)	(1.29)	(0.86)	(0.84)	(1.15)	(1.50)
Natural (-2) – Artificial (2)	-1.34	-1.66	-1.34	-1.40	-1.5	1.08
	(1.22)	(0.82)	(1.00)	(1.07)	(1.09)	(1.54)
Cheap (-2) – Expensive (2)	-0.02	0.12	0.28	0.04	0.24	0.52
	(1.02)	(0.98)	(1.18)	(0.97)	(1.02)	(1.27)
Pleasant (-2) – Unpleasant (2)	-1.10	-1.68	-1.70	-1.54	-1.62	-0.40
	(0.97)	(0.62)	(0.58)	(0.73)	(0.70)	(1.51)
Dislike (-2) – Like (2)	0.92	1.38	1.44	1.40	1.44	0.48
	(1.21)	(0.92)	(0.86)	(0.88)	(0.93)	(1.45)

Mean scores and standard deviations for all pairs of descriptors and handrail samples in the tactile-visual task are presented below (Table 3). Scores from the tactile-visual task are similar to the scores from the tactile task. All wooden handrails were perceived as somewhat warm, dry, and soft. The perceived roughness in wooden handrails ranged from neither smooth or rough to somewhat smooth. Compared to wood, steel handrail was perceived as smoother, colder, damper and harder. All samples of wood were perceived as somewhat/considerably matte, while steel was perceived as somewhat shiny. Perceptions of darkness varied between the samples – stainless steel, unmodified spruce and pine, and acetylated radiata pine were perceived as somewhat/considerably light, while thermally modified spruce and pine were perceived as somewhat dark. All wooden samples were perceived as neither cheap or expensive, somewhat usual, somewhat/considerably natural, pleasant and liked, while the steel sample was perceived as somewhat usual, artificial, and expensive; in the middle/somewhat pleasant and liked.

Table 3: Tactile-visual task scores – M(SD)

	Spruce	Pine	A.Pine	T.M.Pine	T.M.Spruce	Steel
Rough (-2) – Smooth (2)	-0.36	0.00	1.64	0.34	1.10	1.86
	(1.08)	(1.20)	(0.75)	(1.02)	(0.99)	(0.64)
Warm (-2) – Cold (2)	-0.98	-0.92	-1.06	-1.04	-1.26	1.44
	(1.04)	(0.99)	(0.98)	(1.12)	(0.88)	(0.81)
Dry (-2) – Damp (2)	-1.42	-1.48	-1.66	-1.46	-1.62	-0.98
	(0.76)	(0.89)	(0.66)	(0.84)	(0.73)	(1.30)
Soft (-2) – Hard (2)	0.64	0.64	0.72	0.74	0.88	1.88
	(1.37)	(1.40)	(1.41)	(1.35)	(1.36)	(0.44)
Unusual (-2) – Usual (2)	1.06	1.16	1.22	1.32	1.28	0.82
	(1.32)	(1.17)	(1.17)	(1.04)	(1.07)	(1.45)
Natural (-2) – Artificial (2)	-1.66	-1.66	-1.3	-1.34	-1.34	0.98
	(0.75)	(0.87)	(1.22)	(1.32)	(1.10)	(1.57)
Cheap (-2) – Expensive (2)	-0.2	-0.10	0.06	0.04	0.32	1.02
	(1.09)	(1.20)	(1.10)	(1.09)	(1.20)	(1.08)
Pleasant (-2) – Unpleasant (2)	-1.4	-1.64	-1.52	-1.52	-1.76	-0.62
	(0.83)	(0.80)	(0.81)	(0.91)	(0.56)	(1.29)
Dark (-2) – Light (2)	1.58	1.44	1.24	-0.7	-0.96	1.24
	(0.78)	(0.70)	(0.82)	(0.84)	(0.86)	(0.87)
Shiny (-2) – Matte (2)	1.52	1.52	1.44	1.62	1.34	-1.34
	(0.93)	(0.76)	(0.84)	(0.73)	(1.06)	(0.87)
Dislike (-2) – Like (2)	1.04	1.40	1.36	1.16	1.22	0.56
	(1.21)	(0.90)	(0.92)	(1.08)	(0.89)	(1.46)

Ranking task results are presented below (Table 4). For each sample, we calculated the sum of all ranks received from participants. We reranked the samples according to these sums - the handrails with lower sums received higher rankings. The highest ranked material was thermally modified spruce, followed by acetylated radiata pine, untreated pine, and thermally modified pine. The two materials with the lowest ranking were stainless steel and unmodified spruce.

Table 4: Ranking task scores

	Spruce	**Pine**	**A.Pine**	**T.M.Pine**	**T.M.Spruce**	**Steel**
Rank	6	3	2	4	1	5

The Pearson correlation coefficients were calculated for each pair of descriptors within the tactile task (Table 5). Handrails that were rated as less liked were rated as more unusual (r = 0.35, $p < 0.01$), but less warm (r = -0.36, $p < 0.01$), dry (r = -0.28, $p < 0.01$), natural (r = -0.34, $p < 0.01$), and pleasant (r = -0.74, $p < 0.01$).

Table 5: Correlations among descriptors within the tactile task

	Rough	Warm	Dry	Soft	Unusual	Natural	Expensive	Pleasant	Like
Rough	-								
Warm	.28**	-							
Dry	.03	.40**	-						
Soft	.26**	.20**	-.11	-					
Unusual	.06	-.28**	-.29**	.11	-				
Natural	.24**	.56**	.30**	.14*	-.31**	-			
Cheap	.16**	.14*	.02	.16**	-.12*	.09	-		
Pleasant	-.06	.47**	.29**	.00	-.29**	.43**	.00	-	
Dislike	.11	-.36**	-.28**	.05	.35**	-.34**	.07	-.74**	-

** p < .05, ** p < .01*

The Pearson correlation coefficients calculated for each pair of descriptors within the tactile-visual task are presented below (Table 6). Handrails that were rated as less liked were also perceived as less warm (r = -0.40, $p < 0.01$), dry (r = -0.30, $p < 0.01$), natural (r = -0.28, $p < 0.01$), pleasant (r = -0.67, $p < 0.01$), and more unusual (r = 0.34, $p < 0.01$) and shiny (r = 0.25, $p < 0.01$).

Table 6: Correlations among descriptors within the tactile-visual task

	Rough	Warm	Dry	Soft	Unusual	Natural	Cheap	Pleasant	Dark	Shiny	Dislike
Rough	-										
Warm	.13*	-									
Dry	-.11	.36**	-								
Soft	.22**	.24**	-.08	-							
Unusual	.08	-.28**	-.27**	.07	-						
Natural	.21**	.56**	.24**	.22**	-.21**	-					
Cheap	.21**	.20**	-.04	.32**	.02	.21**	-				
Pleasant	.00	.49**	.38**	.08	-.38**	.40**	-.06	-			
Dark	.00	.15*	-.01	.05	-.02	.05	-.05	.06	-		
Shiny	-.34**	-.64**	-.22**	-.20**	.20**	-.57**	-.29**	-.41**	-.11	-	
Dislike	.09	-.40**	-.30**	-.04	.34**	-.28**	.07	-.67**	-.02	.25**	-

** p < .05, ** p < .01*

Correlations between the same pairs of descriptors in the tactile and the tactile-visual task are presented below (Table 7). Correlations among all descriptors between the tactile and tactile-visual task are medium to large in size. This suggests that touch plays an important role in the perception and evaluation of materials even when the materials can be examined visually.

Table 7: Correlations among the same descriptors between the tactile and the tactile-visual task

Rough	Warm	Dry	Soft	Unusual	Natural	Cheap	Pleasant	Dislike
.68**	.71**	.49**	.60**	.34*	.60**	.48**	.53**	.53**

** p < .05, ** p < .01*

CONCLUSIONS

In this study, we examined the perception and evaluation of modified wood compared with untreated wood and stainless steel. Our results indicate that modified wood is perceived and evaluated similarly as untreated wood, while the perception and evaluation of steel differs from all types of wood. Compared to steel, all types of wood received higher overall preference ratings in both the tactile and tactile-visual task. In the ranking task, wood generally received higher ranks than steel, and modified wood was on average rated higher than untreated wood. Results also indicate that touch can have an important role in the perception and evaluation of materials, as the correlation between the tactile and visual-tactile tests were very strong. Taken together, the findings of this study suggest that modified wood possesses tactile and visual features that are liked among older adults. These findings encourage further usage of modified wood in indoor environments. Using handrails manufactured from modified wood would not only decrease the usage of non-renewable materials, but also put older adults in frequent contact with the materials they prefer.

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Valorization of Beech Wood through Development of Innovative Friendly Environmentally Chemical Modification Treatments

Mahdi Mubarok [1,2], Stéphane Dumarcay[1], Holger Militz[2], Philippe Gérardin[1]

[1] LERMAB, Faculté de Science et Technologie, Université de Lorraine, Nancy, France
[Philippe.Gerardin@univ-lorraine.fr]

[2] Wood Biology and Wood Technology, Göttingen University, Germany [hmilitz@gwdg.de]

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ABSTRACT

A comparative study of some wood chemical modification combined with thermal treatments has been examined. European beech (*Fagus sylvatica*), known for its poor natural durability and low dimensional stability, was treated to improve its quality. Three types of additives based on 10% aqueous solution of vinylicpolyglycerol or vinylicglycerol derivatives, and maleic anhydride were impregnated into beech wood, followed by a thermal treatment at 150, 200, and 220°C under inert condition. Treated and untreated wood were then analysed for their mass changes after curing process (Δm), mass loss due to leaching (WL_L), anti-swelling efficiency (ASE), modulus of elasticity (MOE)/modulus of rupture (MOR) and decay resistance against *Coriolus versicolor* (CV) before and after leaching. The main results of this research revealed that the synergic effects of the applied chemical and thermal treatments at 200°C could improve wood dimensional stability up to 62 – 69% and the decay resistance before and after leaching to very durable class (EN BS 350-2 1994) compared to untreated wood, however MOE/MOR values decreased by 17 – 26%/43 – 53%. As a response to the increasing environmental pressure since a decade ago, these treatments could also be used as non-biocide wood preservation treatment.

INTRODUCTION

Non-biocide wood preservation system has been researched for several decades. In general, this system can be separated into two types, thermal and chemical modification, as reviewed by Gérardin (2016). Thermal treatment of wood is one of the alternative processes that have been widely studied and even applied in industrial scale to overcome the problem of wood dimensional stability (Tjeerdsma *et al.* 1998; Militz 2002; Esteves and Pereira 2009; Rowell *et al.* 2009) and biological durability (Kamdem *et al.* 2002; Hakkou *et al.* 2006; Rowell *et al.* 2009). On the other hand, chemical modifications involving impregnation of active chemical into the wood can also be an alternative to overcome those problems (Rowell *et al.* 2009; Militz *et al.* 2011) and even some of them generated products with better characteristic than thermal treated wood (Epmeier *et al.* 2004). Moreover, chemical treatments can be applied at lower temperature, minimizing the degradation of wood compared to thermal treatment. Unfortunately, some of these techniques sometimes need very reactive chemicals/additives, some of which require high concentration chemicals or use of organic solvent during the application. This causes a high cost for the application, which will become a decisive parameter.

In an attempt to find alternatives for easy applied wood modification systems and minimize the costs there are recent investigations on comparative studies of some wood chemical modification treatments based on the utilization of low concentration waterborne solution of vinylicpolyglycerol (Roussel *et al.* 2001; Salman *et al.* 2017) and the new developed formulation based on vinylicglycerol and maleic anhydride. The use of glycerol was based on the thought that it has similar characteristics with already used polyglycerol (PG3) and that it presents a better availability. Both Glycerol and PG3 are renewable chemicals derived from oilseeds easily available as industrial byproducts from soap manufactures and biodiesel production, which could minimize the utilization of petroleum-based chemicals. In order to know their reactivity with the wood and the properties of modified wood, a combination of varied thermal treatments (150, 200, 220ºC) under inert condition was performed to investigate synergic effect on the way for generating the best modified wood performance. These type of combined chemical/thermal modifications have been studied recently based on highly concentrated additives made from *in situ* formation of citric acid and glycerol (Essoua *et al.* 2016) and maleic anhydride alone (Geraud *et al.* 2015) into pine wood, yet the use of low concentation of additives combined with thermal treatment into European beech wood has not been studied. Ultimately, the general goal of this study is also to develop a non-biocide wood preservation system.

MATERIAL AND METHOD

Additive formulation

Polyglycerol-maleic anhydride/PG-MA was made according to Roussel *et al.* (2001) method. 1 mol of polyglycerol (PG3, MR = 242 g/mol) was reacted with 2 mol of maleic anhydride (MA, MR = 98.06 g/mol) and heated at 80°C for 3 h. The reaction was then stopped after disappearance of ATR-FTIR absorption of anhydride and a complete appearance of a characteristic ester band at about 1715 cm^{-1}. The product was directly used without further purification and dissolved into distillated water so that the final concentration of impregnating solution (additive solution) was 10% w/w. Glycerol-maleic anhydride/Gly-MA additive was also made by the same mol comparison and condition as PG-MA. Maleic anhydride/MA additive was made by directly dissolving maleic anhydride into distillated water so that the final solution concentration was 10%w/w.

Wood modification

Oven-dried beech wood samples measuring 3 × 1.5 × 0.5 and 19 × 2 × 0.5 cm^3 (L x R x T) were weighed and placed under vacuum condition (80 – 100 mbar for 10 minutes) in an autoclave (Figure 1) followed with impregnation process with 10%w/w aqueous additive solution for 30 min under vacuum. Afterwards, the pressure was liberated up to 1 bar, the samples were then placed under pressure (10 – 12 bar) for 30 min, and then the pressure was turned down to 1 bar. The samples were then placed under vacuum again (5 – 10 mbar for 10 min), returned back to 1 bar pressure, place to general vacuum (70 – 100 mbar for 1 h), and finally the pressure was liberated to 1 bar. Samples were then removed and air conditioned for 24 hours, dried at 103°C and weighed until constant mass so that their mass changes (Δm) could be calculated (Eqn. 1). Dried impregnated samples were then divided by four groups, one group (dried at 103°C only) was kept, and the remaining three groups were exposed each at 150, 200, and 220°C for 20 h under nitrogen condition. All modified wood were then reweighed for their mass changes (Δm) after thermal treatment. General analysis for modified wood were also performed, such as leaching test (Eqn. 2 & 3), anti-swelling efficiency (ASE), mechanical test (MOE/MOR), and decay resistance test for the different samples before and after leaching. The same procedure was also conducted for untreated samples/control.

Figure 1: Autoclave for vacuum-pressure impregnation and thermal treatment

$$\Delta m\ (\%) = 100 \times (M_1 - M_0)/M_0 \quad (1)$$

where Δm is the mass change after curing process at 103, 150, 200, or 220°C, M_1 is the mass of treated wood at 103, 150, 200, or 220°C and M_0 is the initial mass of wood before modification.

$$\Delta m\ AL = 100 \times (M_2 - M_0)/M_0 \quad (2)$$

where Δm AL is the mass change after leaching process, M_2 is the dry mass of additive-treated or untreated wood at each curing condition after leaching process.

$$WL_L = 100 \times (M_1 - M_2)/M_1 \quad (3)$$

where WL_L is the mass loss due to the leaching test.

RESULTS AND DISCUSSION

Mass changes (Δm) analysis

Table 1 shows that the mass changes (Δm) values decreased as the curing temperature increases. At 103°C, the polarity of PG-MA and Gly-MA additives was the reason of similar Δm values of the treated wood. On the other hand, the absence of hydroxyl group and the less polar double bond of the MA additive system led to the less bulking effect of wood cell wall. Therefore, Δm values of MA-treated wood were lower than that of PG-MA and Gly-MA-treated wood.

At 200 and 220°C, MA-treated wood had the lowest mass changes values and the highest mass loss during thermal treatment. These modification conditions could be explained by the instability of MA-treated wood due to higher acidity of the treatment compared to other treatments with polyols leading to esters formation (Bodirlau *et al.* 2008; Geraud *et al.* 2015). Higher temperatures (>180 - 200°C) and the long duration of treatment (20 h) or combination of both factors are also the origin of accelerated heat-induced wood degradation.

Table 1: mass change, mass change after leaching test, mass loss due to leaching, and 3rd cycle of anti-swelling data at different curing conditions

T(°C)	Additives 10%	Δm[a](%)	Δm AL[b] (%)	WL_L[b] (%)	3rd Cycle ASE[c]
103	PG-MA	10.3 (1.2)	2.0 (0.4)	7.3 (0.9)	46.1 (2.1)
	Gly-MA	10.0 (0.9)	2.2 (0.4)	6.8 (0.5)	46.5 (4.9)
	MA	9.3 (0.7)	2.2 (0.7)	6.4 (0.9)	41 (2.8)
	Control	0	-1.4 (0.3)	1.4 (0.3)	13.9 (8.0)
150	PG-MA	8.8 (1.0)	5.6 (1.0)	2.5 (0.6)	48.1 (4.6)
	Gly-MA	8.6 (0.8)	4.6 (0.4)	4.0 (0.4)	55.0 (4.5)
	MA	7.2 (0.8)	1.4 (0.8)	5.3 (0.8)	47.7 (3.3)
	Control	-0.1 (0.2)	-1.8 (0.2)	1.7 (0.3)	21.6 (6.3)
200	PG-MA	3.8 (1.6)	0.9 (1.5)	2.3 (0.9)	61.7 (3.2)
	Gly-MA	1.1(1.0)	-0.8 (1.9)	2.6 (1.2)	69.0 (4.6)
	MA	-4.3 (0.5)	-7.7 (0.6)	3.7 (0.7)	66.9 (9.0)
	Control	-2.6 (0.5)	-4.2 (0.3)	1.7 (0.1)	49.4 (2.5)
220	PG-MA	-3.2 (1.2)	-5.4 (1.2)	2.4 (0.6)	74.7 (4.4)
	Gly-MA	-5.7 (1.2)	-9.0 (1.1)	3.6 (0.4)	78.2 (1.9)
	MA	-9.9 (0.8)	-13.8 (0.9)	4.2 (1.3)	66.7 (2.2)
	Control	-10.5 (0.8)	-11.6 (1.0)	1.2 (0.3)	63.5 (2.3)

[a]Each value was based on the average of ninety six samples at 103°C and twenty four samples for each thermal treatment (150, 200, 220°C), [b]Each value was based on the average of six samples, [c]Each value was based on the average of four samples. Standard deviation is in parentheses

Leaching analysis

Leaching test referred to procedure adapted from NF X 41-569 standard (2014). According to the leaching data in the Table 1, percentage of mass loss of additive-treated and untreated wood after leaching/WL_L (Eqn. 3) decreased by the increase of curing temperature.

At 150°C curing condition, almost all treated wood have higher mass changes after leaching values/Δm AL (Eqn. 2) than other curing conditions. It indicates that at this curing temperature the PG-MA and Gly-MA additives have begun to fix better into the wood than at 103°C curing condition and the problem of heat-induced degradation of the additive and wood was minimal. Therefore, mass losses of the additives treated wood after leaching (WL_L) were also decreased. On the other hand, even at higher curing temperatures, MA-treated wood remains with a lower Δm AL and the highest WL_L values. The reaction between water and unreacted MA to form soluble maleic acid during leaching process was the most possible factor for this problem. Some possible factors presented in Δm analysis previously were also might contribute to the leaching character of this MA-treated wood.

At higher curing condition (200 and 220°C), the reduction of mass changes for both before and after leaching (Δm AL) caused by heat-induced wood degradation emerged. These conditions made a better additive fixation into the wood, and WL_L values were also diminished, especially at 200°C curing condition.

Anti-swelling efficiency (ASE)

ASE test referres to drying-wetting cycle system adapted from Pfriem *et al.* (2012). Based on the Table 1, all ASE values increased with the increase of curing temperature, with the additive-treated woods presenting higher ASE values than control. This indicates that there were some chemical (*e.g.* reaction between additives and components in wood cell wall, degradation of hemicellulose) and physical interactions (*e.g.* anchoring system of the cured additives into wood cell wall, the increase in surface tansion) due to the high temperature curing. These ASE results were similar some previous research (Iwamoto and Itoh 2005), where maleic anhydride treated wood had ASE values > 40% in the first drying-wetting cycle.

Modulus of elasticity (MOE) and modulus of rupture (MOR) analysis (EN 310 1993)

Based on the results in Table 2, both MOE and MOR values of the additive-treated wood were lower than control at all curing conditions. Each additive-treated wood had MOE/MOR values which were proportionally approximate with their Δm values. MOE values decreased gradually as the curing temperature increased.

Table 2: MOE/MOR values of treated and untreated wood and MOE/MOR reduction values compared to untreated wood at different curing condition

T (°C)	Additives 10%	Δm (%)*	MOE (N/mm^2) / MOE Red (%)*	MOR (N/mm^2) / MOR Red (%)*
103	PG-MA	9.1 (0.4)	9479 (1089) / -23.9	96 (19) / -27.5
	Gly-MA	9.3 (0.4)	9205 (876) / -26.1	89 (11) / -32.6
	MA	8.4 (0.4)	10070 (971) / -19.2	80 (16) / -39.4
	Control	0.0 (0.0)	12460 (1390) / 0.0	133 (17) / 0.0
150	PG-MA	8.0 (0.3)	10723 (748) / -13.9	89 (11) / -33.2
	Gly-MA	8.2 (0.3)	10393 (946) / -16.6	85 (15) / -35.9
	MA	5.9 (0.4)	10916 (850)/ -12.4	75 (6) / -43.3
	Control	-0.4 (0.0)	12801 (1243) / 2.7	135 (18) / 1.6
200	PG-MA	3.7 (0.8)	10329 (960) / -17.1	75 (10) / -43.4
	Gly-MA	-0.0 (1.3)	9283 (1382) / -25.5	64 (13) / -51.9
	MA	-2.5 (0.8)	9760 (1663) / -21.7	62 (15) / -52.9
	Control	-3.6 (0.4)	12934 (2047) / 3.8	102 (20) / -22.7
220	PG-MA	-8.7 (0.7)	9255 (1049) / -25.7	54 (13)/ -59.3
	Gly-MA	-12.1 (2.2)	9318 (1523) / -25.2	55 (27) / -58.9
	MA	-10.7 (0.9)	9701 (1025) / -22.1	54 (10) / -59.2
	Control	-17.5 (0.9)	9441 (3761) / -24.2	52 (21) / -60.7

*Each value was based on the average of ten samples; standard deviation is in parentheses

On the other hand, MOE of treated wood increased slightly at 150°C curing condition, even though these increments were not significant compared to the samples at 103 and 200°C. The higher positive mass changes after leaching (Δm AL) (Table 2) at this temperature indicated that the interaction between additive and wood had been well constructed by minimizing the heat-induced mechanical degradation of wood.

In addition, the low concentration of applied additive solution might contribute for the small differences in their mechanical properties, especially among additive-based woods. Compared to untreated wood and thermal treated controls, the acidic properties of the applied additives solution in the additive-treated wood might contribute to destabilize or even to hydrolyse some glycosidic bond of hemicellulose and amorphous cellulose, which eventually would reduce the mechanical properties (e.g MOE and MOR) of wood. Nevertheless, both thermal treated control and additive-treated wood gave a similar respond on those mechanical properties at 220°C curing condition.

Decay resistance analysis (EN 113 1996)

In general, durability values (EN BS 350-2 1994) of both treated and untreated wood against *Coriolus versicolor* (CV) attacks increased (mass loss decreased) by the increase of curing temperature (Table 3). At 200°C, all treated wood with additives for before and after leaching had lower mass loss values against CV (Class 1, very durable) than control (Class 3, moderately durable). These phenomena indicated that in this curing condition, the synergic effect of both applied chemical and thermal modification gave better decay durability properties of modified wood than at lower curing conditions.

Table 3: Mass losses and durability due to decay test against Coriolus versicolor for treated and untreated wood at different curing condition before and after leaching

T (°C)	**Additives 10%**	**Before Leaching[a]**		**After Leaching[b]**	
		Δm (%)	**MLDB (%) / Durability Class**	**Δm AL (%)**	**MLDA (%) / Durability Class**
103	PG-MA	10.6 (2.2)	7.6 (1.1) / 3	3.6 (0.7)	24.1 (5.2) / 3
	Gly-MA	9.7 (1.3)	7.8 (0.6) / 3	4.4 (0.8)	29.3 (6.0) / 4
	MA	8.9 (1.2)	9.50 (0.9) / 3	2.8 (0.4)	6.6 (0.6) / 2
	Control	0.0 (0.0)	24.2 (2.6) / 5	-1.0 (0.2)	42.4 (7.3) / 5
150	PG-MA	8.7 (1.02)	5.3 (3.1) / 2	6.2 (1.3)	32.7 (3.2) / 4
	Gly-MA	8.2 (1.10)	3.5 (0.4) / 1	6.3 (0.6)	21.4 (1.9) / 3
	MA	7.0 (0.4)	7.7 (0.8) / 3	1.2 (0.7)	6.2 (0.5) / 2
	Control	-0.2 (0.2)	21.2 (1.4) / 4	-0.9 (0.1)	41.8 (7.5) / 5
200	PG-MA	4.1 (1.6)	0.9 (0.5) / 1	-1.0 (1.1)	3.1 (3.0) / 1
	Gly-MA	0.6 (1.0)	0.32 (0.3) / 1	-1.2 (2.7)	0.7 (0.8) / 1
	MA	-4.5 (0.2)	0.1 (0.4) / 1	-8.5 (1.1)	0.8 (0.3) / 1
	Control	-2.3 (0.2)	14.0 (2.4) / 3	-6.8 (0.3)	21.3 (2.6) / 3
220	PG-MA	-2.8 (1.2)	0.0 (0.2) / 1	-6.7 (3.1)	-0.4 (0.2) / 1
	Gly-MA	-6.2 (1.1)	-0.3 (0.2) / 1	-6.8 (1.4)	-0.2 (0.2) / 1
	MA	-9.8 (0.8)	-0.5 (0.1) / 1	-13.5 (1.1)	0.4 (0.2) / 1
	Control	-10.3 (0.8)	1.7 (1.2) / 1	-13.7 (0.4)	1.6 (0.9) / 1

[a] Incubation process in five weeks and each value was the average of six samples; [b] Incubation process in twelve weeks and each value was the average of five samples; MLDB = mass loss after decay test for treated and untreated wood before leaching process; MLDA = mass loss after decay test for treated and untreated wood after leaching process; Durability class referred to N BS 350-2 1994 regulation (1= very durable, 2= durable, 3= moderately durable, 4=slightly durable, 5= non durable); standard deviation is in parentheses

These results corroborate the previous research from Salman *et al.* (2017), which revealed that a significant decrease in mass loss of PG-MA-treated wood against CV began at 200°C curing condition. On the other hand, Iwamoto and Itoh (2005) and Geraud *et al.* (2015) also quoted that MA-treated wood cured at 180°C had better decay resistance than at lower curing condition. Furthermore, thermal treatment at 220°C gave best results on this decay resistance for all additive-treated and untreated wood before and after leaching. Thus at 220°C, thermal modification of wood played dominant rule in this condition.

CONCLUSION

Based on the results, some additive-treated wood have shown their properties improvement by the increase of curing temperature compared to untreated wood. The synergic effect of thermo-chemical modification was observed at 200°C. PG-MA, Gly-MA, and MA-treated wood presented better improvement in dimensional stability (62 – 69%) and decay durability for before and after leaching process (Class 1, very durable) against *Coriolus verisicolor* than the control. Unfortunately, at this temperature, MOE/MOR values decreased by 17 – 26%/43 – 53% compared to untreated wood. Nevertheless, these non-biocide wood preservation treatments results could be the basis for further work and other advanced analytical tests.

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Infrared spectroscopy and chemometric methods for the evaluation of the thermal/chemical treatment effectiveness of hardwoods

Carmen-Mihaela Popescu[1,2], Davor Kržišnik[3], Miha Hočevar[3], Miha Humar[3], Nejc Thelar[3], Maria-Cristina Popescu[1], and Dennis Jones[4,5]

[1]Petru Poni Institute of Macromolecular Chemistry, Iasi, Romania [email: mihapop@icmpp.ro, cpopescu@icmpp.ro]
[2]Centre of Wood Science and Technology, Edinburgh Napier University, Edinburgh, UK
[3]Biotechnical Faculty,University of Ljubljana, Jamnikarjeva 101, 1000 Ljubljana, Slovenia [email: davor.drzisnik@bf.uni-lj.si, miha.humar@bf.uni-lj.si, nejc.thaler@bf.uni-lj.si]
[4]DJ Timber Consultancy Ltd, 15 Heol Pen Y Coed, Neath, SA11 3SP, United Kingdom [email: dr_dennisjones@hotmail.co.uk]
[5]Wood Science and Engineering, Luleå University of Technology, Forskargatan 1, S-93197 Skellefteå, Sweden [email: dennis.jones@ltu.se]

Keywords: beech wood, hierarchical cluster analysis, infrared spectroscopy, principal component analysis, thermal/chemical treatment

ABSTRACT

In this study were investigated the combined effects of chemical treatments (such as tricine and bicine) with thermal modification. The modifications which appear in the wood structure were evaluated by infrared spectroscopy and chemometric methods (principal component analysis and hierarchical cluster analysis). After the treatment about 6-7 % of WPG was identified in treated samples, but further thermal treatment decreased the WPG to about 5%. The modifications appearing in the spectra were mostly related to increase of the intensities of the bands assigned to C=O groups but also to N-H and C-N groups, with shifting of some bands to higher wavenumber values.

INTRODUCTION

Wood is an important natural resource used in many applications from constructions and engineered products to different tools and artworks. Despite of its numerous advantages, it presents some limitations such as: dimensional instability, susceptibility to fungal decay or weathering, etc (Popescu *et al*. 2014, Hauptmann *et al*. 2015). In order to prevent these, thermal (i.e. Herrera-Díaz *et al*. 2017, Korkut *et al*. 2012, González-Penã *et al*. 2009) or chemical treatments (Jebrane *et al*. 2011, Marfo *et al*. 2017, Kumar *et al*. 2018) have been applied.

The thermal modification of wood has been well established over the past decades, with several commercialised processes. This type of treatment causes transformations in its composition, through a series of hydrolysis, oxidation and decarboxylation reactions coupled with heat and mass transfer and physical changes (conformational changes and molecular rearrangements). Chemical reactions involved during wood heat treatment as well as the final properties of the material depend directly on the treatment temperature, relative humidity, treatment time and by the nature of the wood species used (Popescu *et al*. 2013). Even the resulted end product present improved physical characteristics, like lower hygroscopicity, better dimensional stability, durability of the wood if it is to be exposed to different chemicals or biological agents such as fungi and bacteria, or to frequent use under natural environmental conditions, the mechanical properties are often reduced.

Another possible type of wood modification is the reaction with different chemicals – chemical modification, where chemical moieties are covalently bonded to the wood cell wall polymers. Different chemical modifications (Jebrane *et al*. 2011, Marfo *et al*. 2017, Kumar *et al*. 2018, Hill *et al*. 2004, Ozmen *et al*. 2006, Hill 2006) can be applied to change the properties of wood (Hill 2006), especially to improve the dimensional stability, decay resistance and water sorption of wood, and better mechanical properties (Mai and Militz 2004).

As a result of this modification method, the hydroxyl groups in the cell wall are substituted partially and the cell wall of the wood is bulked with the bonded chemicals. The substitution of the hydroxyl groups reduces the number of primary sorption sites (which are generally assumed to be the OH groups); while the bulking reduces the volume in the wood cell wall which is available to water molecules. The most common chemical modification process involved reaction with anhydrides. Although in literature can be found many different anhydrides used, acetylation using acetic anhydride is the most studied and is also produced commercially (Popescu *et al*. 2014).

Apart of anhydrides, many other chemicals have been used to try to improve the properties of wooden material. Foe example treatments with dimethylol dihydroxyethylene urea (DMDHEU), melamine resin, silane or silicon polymers were found to improve the mechanical strength of wood (Hauptmann *et al*. 2015).

More recently, the use of Maillard reactions for wood treatment proved to be promising modification method to improve some of the wood properties.

In this context, a recent work of Hauptmann and co-workers (Hauptmann *et al*. 2015) has considered the use of tricine for the modification of wood. This is capable of binding with reduced sugars, though studies have been limited to a maximum temperature of 103 ºC. They observed increased hardness and tensile strength of their modified wood species.

In another work Peeters and co-workers (Peeters *et al*. 2018) describe preliminary results of their experiments based on a Maillard type of reaction at 120 ºC by using non-toxic chemicals to decrease the wood decay.

Maillard type reactions are a cascade of reactions (known also as non-enzymatic browning). The initial step consists in reaction between a reducing end of a saccharide and an amino acid (Hauptmann *et al*. 2015, Peeters *et al*. 2018). This reaction takes place usually during the heat processing of food with a low relative humidity (Hauser *et al*. 2014), and it is considered to cause the brown stains during wood kiln drying with temperatures higher than 80°C due to the presence of natural amino acids and reduced sugars (Hauptmann *et al*. 2015).

The most efficient characterization method to identify the modifications appearing in the wood structure during heating and to identify the possible interaction and bonds formed between the wood components and the used reagents in chemical modification, is infrared spectroscopy. This technique proved to be an efficient tool to identify small modifications in the wood structure, appearing during different treatments (i.e. Mohebby 2008, González-Penã and Hale 2011, Popescu *et al*. 2013), decay (i.e. Ferraz *et al*. 2000, Popescu *et al*. 2010) or photodegradation (i.e. Popescu *et al*. 2011, Tolvaj *et al*. 2016). Moreover, due to the use of small amount of sample and little or no processing this method is also considered non-destructive.

In the present study we investigated the combined effects of chemical treatment and the thermal modification. To identify and better understand the structural changes appearing during these processes in the wood cell wall, we used infrared spectroscopy, combined with chemometric methods, like principal component analysis and hierarchical cluster analysis.

EXPERIMENTAL

Materials

The materials used in this study were beech (*Fagus sylvatica*) wood blocks, bicine [2- (Bis (2-hydroxyethyl) amino) acetic acid] (Figure 1a) and tricine [N- (2- Hydroxy- 1,1- bis (hydroxymethyl) ethyl) glycine] (Figure 1b).

a. ***b.***

Figure 1: Chemical structure of bicine (a) and tricine (b)

Treatment

The wood samples were separated in six categories as follows:
1 – control/reference samples (A)
2 – thermal treated wood samples at 160 ^{o}C (B)
3 – bicine impregnated wood and then dried (C)
4 – bicine impregnated wood followed by thermal treatment at 160 ^{o}C (D)
5 – tricine impregnated wood and then dried (E)
6 – tricine impregnated wood followed by thermal treatment at 160 ^{o}C (F)
After the thermal treatment the mass loss of the samples (B) was about 1.6%. The WPG for the bicine (C) and tricine (E) treated wood samples was 7% and 6%, respectively. For the samples chemically impregnated and thermally treated, the WPG was about 5% for both types of chemicals, bicine (D) and tricine (F).

Methods

The infrared spectra of the reference and treated wood samples were recorded in KBr pellets on a Bruker ALPHA FT-IR spectrometer with 4 cm^{-1} resolution. The concentration of the sample was constant of 2 mg / 200 mg KBr. Processing of the spectra was performed using the Grams 9.1 program (Thermo Fisher Scientific).
Principal component analysis (PCA) and hierarchical cluster analysis (HCA) were performed by using the ChemoSpec package (Hanson 2017) in R software.

RESULTS AND DISCUSSION

The spectra of the control (reference) and treated beech wood samples are presented in Figures 2 and 3.
As can be observed, the spectra maintain the two main regions: 3700 – 2500 cm^{-1} assigned to different stretching vibrations of hydroxyl groups, methyl, methylene and NH groups present both in wood and bicine and tricine and the 1800 – 800 cm^{-1}, also called fingerprint region, where the most important stretching, deformation vibrations of the wood and chemical groups are found.
The spectrum of reference beech wood shows the characteristics bands of the hardwoods, with a large band at about 3420 cm^{-1} assigned to inter and intramolecular hydrogen bonds in the wood components, and the band from about 2870 cm^{-1} assigned to the symmetric and

antisymmetric stretching vibration of the methyl and methylene groups (Popescu *et al*. 2010, Popescu *et al*. 2011, Popescu *et al*. 2013).

When comparing the reference wood spectrum (A) with the thermal treated (B) one, no difference is visible between the two spectra. This is due to the short treatment time, but also because most of the bands represent an envelope of the individual bands, and in normal spectra is not possible to distinguish between small differences appearing in the individual bands.

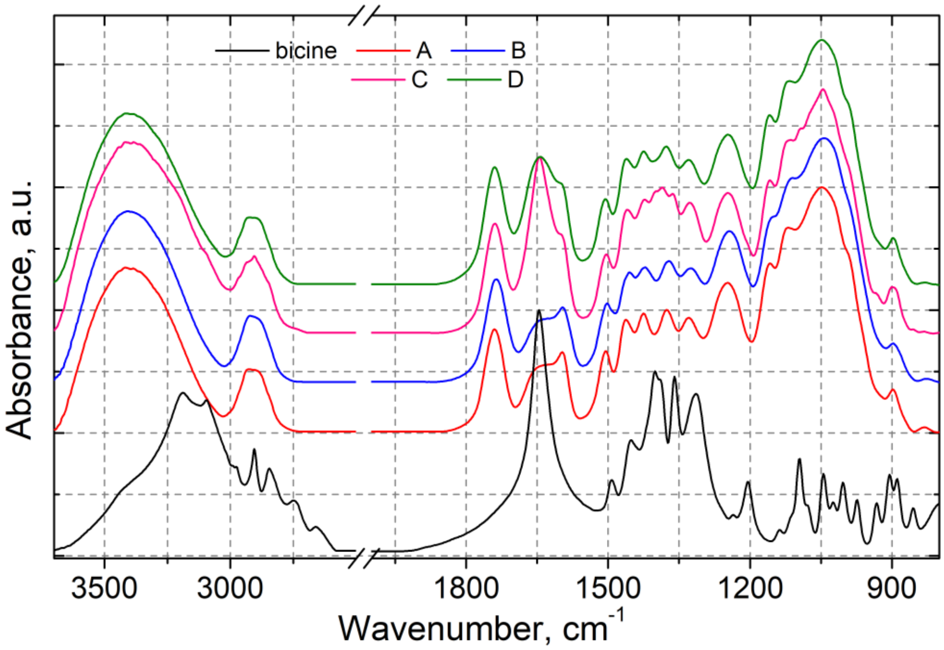

Figure 2. Infrared spectra of untreated, thermal treated and bicine treated beech wood samples

The spectrum of bicine (black line in Figure 2) shows strong absorption bands between 3000 and 2600 cm^{-1}, assigned to stretching vibration of the hydroxyl (from the primary alcohol) groups and methylene groups in bicine; at 1653 cm^{-1} assigned to C=O stretching vibration, 1492 and 1451 cm^{-1} assigned to CH_2 bending vibration, 1401 and 1313 cm^{-1} assigned to stretching vibration of the C-OH from carboxylic acid groups, 1359 cm^{-1} assigned to OH bending vibration in primary alcohol groups, 1205 cm^{-1} assigned to stretching vibration of the C-N groups, 1095 and 1043 cm^{-1} assigned to stretching vibration of C-O from alcohols.

When beech wood is treated with bicine (C) and then dried, the spectrum indicates the presence of the chemical in the structure, showing modifications especially in the 3050 – 2750 cm^{-1} region and also a strong increase of the intensity of the band from 1655 cm^{-1}. When the wood sample is further exposed to temperature in the thermal process, the presence of the modifications in the wood structure are evidenced in the spectrum by the increase of the intensity of the band from 1655 cm^{-1} (comparing to reference and thermal treated wood spectra) and also shifting of some bands maxima to higher wavenumber.

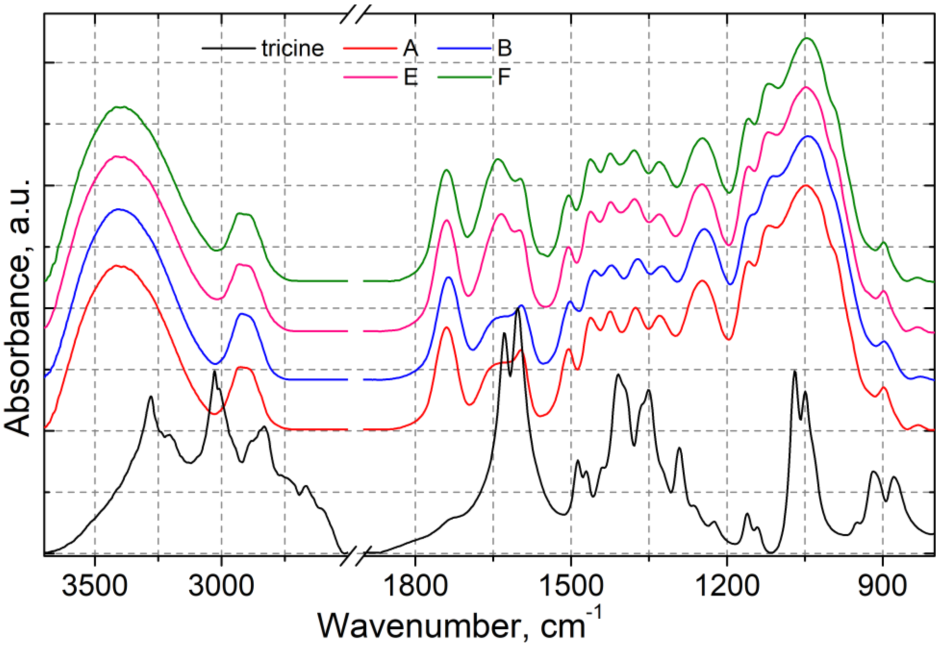

Figure 3. Infrared spectra of untreated, thermal treated and tricine treated beech wood samples

Figure 3 present the spectra of beech wood control and thermal treated combined with tricine and tricine treated wood spectra. In this case, the spectrum of tricine present specific bands at: 1734 cm^{-1} assigned to carboxylic groups, a doublet at 1630 and 1603 cm^{-1} assigned to N-H from the secondary amine groups, 1470 and 1350 cm^{-1} assigned to bending vibration of CH2 groups, 1411 cm^{-1} assigned to OH bending in carboxylic acids, 1290 cm^{-1} assigned to C-O stretching vibration from carboxylic acid groups, 1159 and 1143 cm^{-1} assigned to C-N stretching vibration, 1069 and 1048 cm^{-1} assigned to C-O stretching vibration in primary alcohols.

In the treated wood samples with tricine the presence of amino groups is clearly evidenced by an increase in intensity of the band from 1630 cm^{-1}, and also shifting of the bands to different wavenumber.

Further in order to get more detailed information, chemometric methods (principal component analysis and hierarchical cluster analysis) have been applied.

It is known that principal component analysis gives detailed information regarding the differences which appear between the series of similar samples. In our case, in order to perform the PCA scores the raw spectra of reference and treated beech wood samples were used and they are presented in Figure 4.

The PC1 (principal component factor 1) describes 74% and PC2 (principal component factor 2) 12% of data variance, therefore more than 86% of the existed variances in all spectra can be captured using these two dimensions instead of the initial data.

The bicine treated samples present positive values on PC1, the tricine treated ones have values close to zero while the reference and thermal treated samples present negative scores. On the other side, on PC2, the reference and thermal treated samples present negative scores, while the chemical treated and thermo-chemical treated ones present positive values.

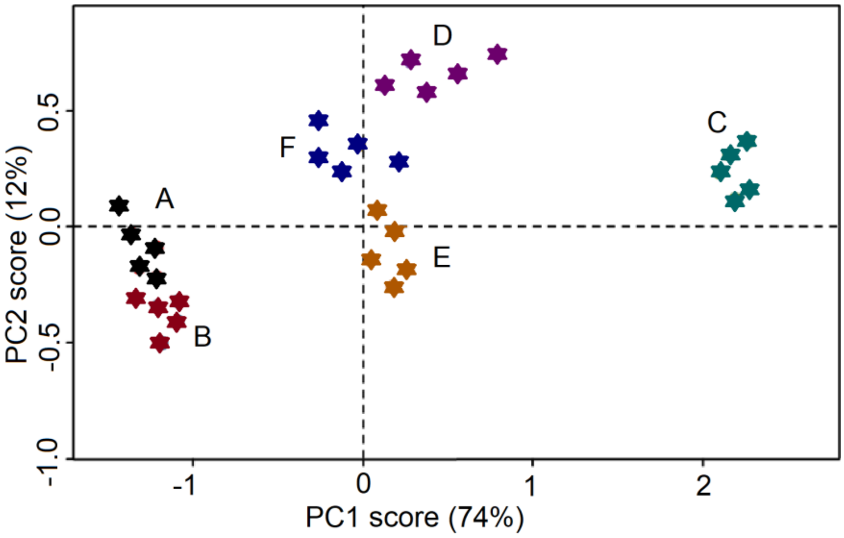

Figure 4. ***PC1 versus PC2 scores plot of the studied beech wood samples***

PC1 is the most informative latent variable for the description of chemical treatments, differentiating the chemical and thermo-chemical treated samples from the control and thermal treated control samples, while PC2 separate the samples according to thermal and non-thermal treatment, indicating the negative relationship between these two series of thermal treated samples.

In addition to principal component analysis, we performed the hierarchical cluster analysis (HCA), which allow us to emphasize the natural grouping in the data set, making possible at the same time to visualize the relationships among different groups. The dendrogram is separated in two main clusters, differentiating between the reference and thermal treated beech wood samples and the chemically and thermo-chemically treated ones (Figure 5).

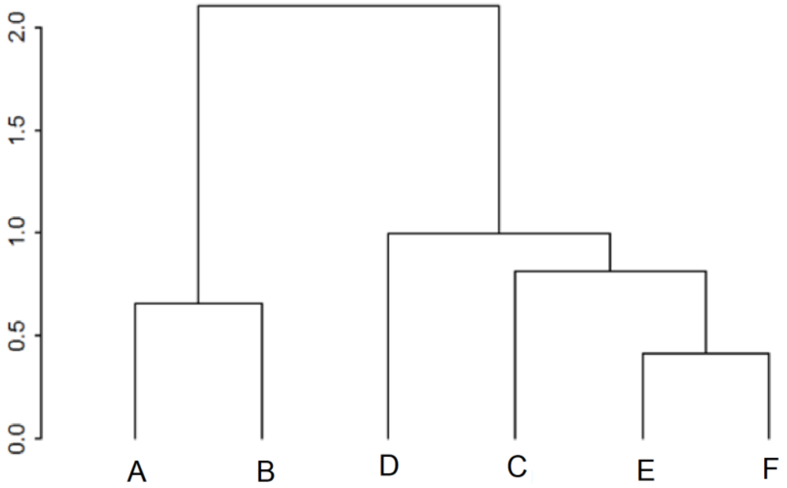

Figure 5. HCA plots of the beech wood samples

The second cluster is divided in several sub-clusters, which discriminate between the bicine and tricine treated samples.

CONCLUSIONS

From the infrared spectroscopy was possible to clearly identify the presence of chemicals in the wood structure. It is likely that the level of treatment used could be excessive for the potential level of Maillard reaction likely to occur, but in this first instance the aim was to demonstrate the potential for reaction, and should evidence of effective treatment be achieved, further work would be warranted on the correct dosage.

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Performance of modified wood in service – multi-sensor and multi-scale evaluation

Anna Sandak[1], Jakub Sandak[2,3,4], Marta Petrillo[5] and Paolo Grossi[6]

[1]CNR-IVALSA, via Biasi 75, 30010 San Michele all'Adige, Italy [email: anna.sandak@ivalsa.cnr.it]
[2]InnoRenew CoE, Livade 6, 6310 Izola, Slovenia [email: Jakub.Sandak@innorenew.eu]
[3]University of Primorska, Faculty of Mathematics, Natural Sciences and Information Technology, Glagoljaska 8, 6000 Koper, Slovenia
[4]CNR-IVALSA, via Biasi 75, 30010 San Michele all'Adige, Italy [email: sandak@ivalsa.cnr.it]
[5]CNR-IVALSA, via Biasi 75, 30010 San Michele all'Adige, Italy [email: petrillo@ivalsa.cnr.it]
[6]CNR-IVALSA, via Biasi 75, 30010 San Michele all'Adige, Italy [email: grossi@ivalsa.cnr.it]

Keywords: service life performance, modified wood, multi-sensor evaluation, weathering, facades

ABSTRACT

The performance of 120 selected façade materials provided by over 30 industrial and academic partners was evaluated during 12-month experimental campaign of natural weathering. A multi-sensor measurement chain for the acquisition of properties at different scales (molecular, microscopic, macroscopic) included both laboratory and on-site techniques. Investigated bio-materials were characterized before, during and after degradation by biotic and abiotic agents in order to provide experimental data to be used for better understanding of the bio-materials performance/degradation as a function of time and/or weather dose. Obtained data were utilized for the development series of numerical models simulating materials appearance changes along the service life of building facade. An original software simulating bio-materials' performance in any geographical location has been developed and is currently under integration with Building Information Modelling. It serves as a tool for demonstrating advantages of using bio-based materials when compared to other commonly utilized alternative resources. Results of the BIO4ever project provide solid technical and scientific knowledge, but also contribute to the public awareness by demonstrating the environmental benefits to be gained from the knowledgeable use of bio-based materials in buildings.

INTRODUCTION

Wood is a traditional material utilized for construction of buildings since beginning of civilisation. Its availability, relatively low maintenance cost and ease of processing, result in the common use as prevalent construction material for both interior and exterior applications. While possessing several advantages, such as aesthetic appeal and positive weight to load-bearing capacity ratio, unprotected wood suffers when exposed to the environmental conditions by changing its dimensions and appearance. The most susceptible parts are unprotected surfaces in outdoor environment, since these are directly subjected to ageing, weathering or decay.

Wood modification processes leads to the enhancement of desired properties by means of chemical, biological or physical agents. Wood properties are essentially determined by its chemical composition, therefore, several modification processes target specific changes of constitutive woody polymers at the molecular level. Nevertheless, some modification processes do not change the chemical composition of wood itself, but focus on the morphological or physical modification (Hill 2006). New developments in the field of wood modification offer assortment of innovative products with highly enhanced properties of natural timber. These include innovative bio-based composite materials, as well as more effective and environmental-friendly protective treatments, e.g. thermal treatment, densification, impregnation and chemical modifications. Similar revolutionary progress is observed with surface treatments including advanced coatings, or integration of nanotechnology developments in wood protection. Today's bio-based building materials, even if well characterized from the technical point of view, are often lacking of reliable models describing their performance during service life. This paper presents summary of the scientific results obtained within framework of BIO4ever project "Bio-materials for building envelope – expected performance, life cycle costing and controlled degradation".

EXPERIMENTAL

Experimental samples

Performance of 120 selected façade materials provided by over 30 industrial and academic partners from 17 countries was evaluated in several experimental configurations. The samples were classified in seven categories, according to the treatment applied: natural wood (or other bio-based material), composites, chemically modified, thermally modified, impregnated, coated and/or surface treatment and hybrid modified. The latest include combination of at least two different treatments (Table 1).

Table 1: Categories of bio-based facades materials tested within BIO4ever project

Modification process	Examples	Number of materials
natural	wood, bamboo	19
chemical	acetylation, furfurylation	5
composites	panels, bio-ceramics, tricoya, wood plastic composites	7
coating & surface treatments	different coatings, carbonized wood, nanocoatings	16
impregnation	DMDHEU, Knittex, Madurit, Fixapret	28
thermal modification	vacuum, saturated steam, oil heat treatment	20
hybrid modification	thermal treatment + coating, thermal treatment + impregnation, acetylation + coating etc.	25

An example of six radiata pine (*Pinus radiata* D.Don) samples representing different commercially available modification processes was selected for the demonstration. Weathering performance of these materials was compared with the not treated wood of scots pine (*Pinus sylvestris* L.), being usually considered as a reference material (Table 2).

Table 2: Description of experimental samples

Sample number	Wood species	Bulk treatment	Surface treatment	Product on the market
09	Radiata pine	thermal treatment + penetrating oil	-	yes
10	Radiata pine	thermal + silicate treatment	-	yes
30	Radiata pine	thermal treatment #1	coating	yes
31	Radiata pine	furfurylation	-	yes
34	Scots pine	-	-	yes
45	Radiata pine	thermal treatment#2	-	yes
51	Radiata pine	acetylation	-	yes

Selected modification processes included: acetylation, furfurylation, thermal treatment with various technologies and thermal treatment combined with impregnation and surface coating. Investigated treatments were classified as chemical, thermal and hybrid modification according to the categories presented in Table 1. All investigated modified materials are commercially available on the market.

Weathering tests

Natural weathering tests were performed in San Michele, Italy, (46°11’15’’N, 11°08’00’’E), in order to provide reference data for simulation of the bio-materials’ performance in a function of the exposure time. Samples were exposed on the vertical stands representing building façade. Stands were oriented to 4 cardinal directions. The weathering experiment was carried out for 12 months and the test is still ongoing. Presented results refer to the southern exposure of samples, with the experiment start in March 2017.

Materials characterization

High resolution photos (Nikon D5500 equipped with lenses Nikor AF-S 35mm) were regularly acquired in a monthly bases to capture the progress of the samples’ appearance change. Additionally, part of exposed samples (three replicas per cycle) was exchanged every 3 months and stored in a climatic chamber before characterization. Materials characterization included scanning with office scanner, as well as measurement of the colour (CIE L*, a*, b*), gloss, roughness (in two cardinal fibre directions), and spectroscopy in VIS, NIR and IR ranges with laboratory and portable spectrometers. The NIR bands were assigned according to Schwanninger *et al*. (2011a).

Table 2: Description of experimental samples

band number	Wavenumber (cm-1)	Wood component	Functional group
1	4198	holocellulose	CH
2	4280	cellulose	CH, CH_2
3	4339	holocellulose	CH
4	4404	cellulose, hemicellulose	CH, CH2, OH, CO
5	4620	cellulose, hemicellulose	OH, CH
6	4686	acetyl groups in hemicellulose	CH_3, C=C, C=O
7	4890	cellulose semi-crystalline and crystalline	OH, CH
8	5219	water	OH
9	5464	cellulose semi-crystalline and crystalline	C=O
10	5587	cellulose semi-crystalline and crystalline	CH
11	5658	unassigned	CH_2
12	5800	hemicellulose (furanose/pyranose)	CH
13	5883	hemicellulose	CH
14	5951	hemicellulose	CH_3
15	5980	lignin	CH
16	6009	hemicellulose	CH
17	6121	cellulose	OH
18	6287	cellulose crystalline	OH
19	6450	cellulose crystalline	OH
20	6722	cellulose semi-crystalline	OH
21	6785	cellulose	OH
22	7008	amorphous cellulose/water	OH
23	7300	hemicellulose	CH_3
24	7418	hemicellulose	CH_3

RESULTS AND DISCUSSION

Materials appearance

The intensity of weathering depends on timber species, architectural design solutions, function of product, finishing technology applied for wood protection, and on the specific local conditions. All experimental samples were prepared from radiate pine and exposed in same climatic conditions for identical period. Therefore, it can be stated that the difference in performance are modification process dependent. The appearance of investigated materials in the function of time is presented in Figure 1. It can be seen that some of the materials are relatively stable regarding colour and pattern changes. The material #10 become lighter after 3 months exposure period. However, according to the technical sheet provided by producers it was desired to “silver off” the surface due to weathering and then maintain that appearance unchanged during service life. Materials #31, #34, #45 and #51 contain noticeable mould discoloration on their surfaces. The visual assets in materials outlook were confronted with changes in colour coordinates. The lightness (*CIE L*) parameter was constant in materials with relatively stable colour (e.g. #09, #30). Even if the weathering test was performed for 12 months, none of investigated materials became grey, corresponding to the usual colour of wood long-term exposed to natural weathering. However, an increase of gloss parameters (especially across the fibres) was observed with the progress of the weathering process.

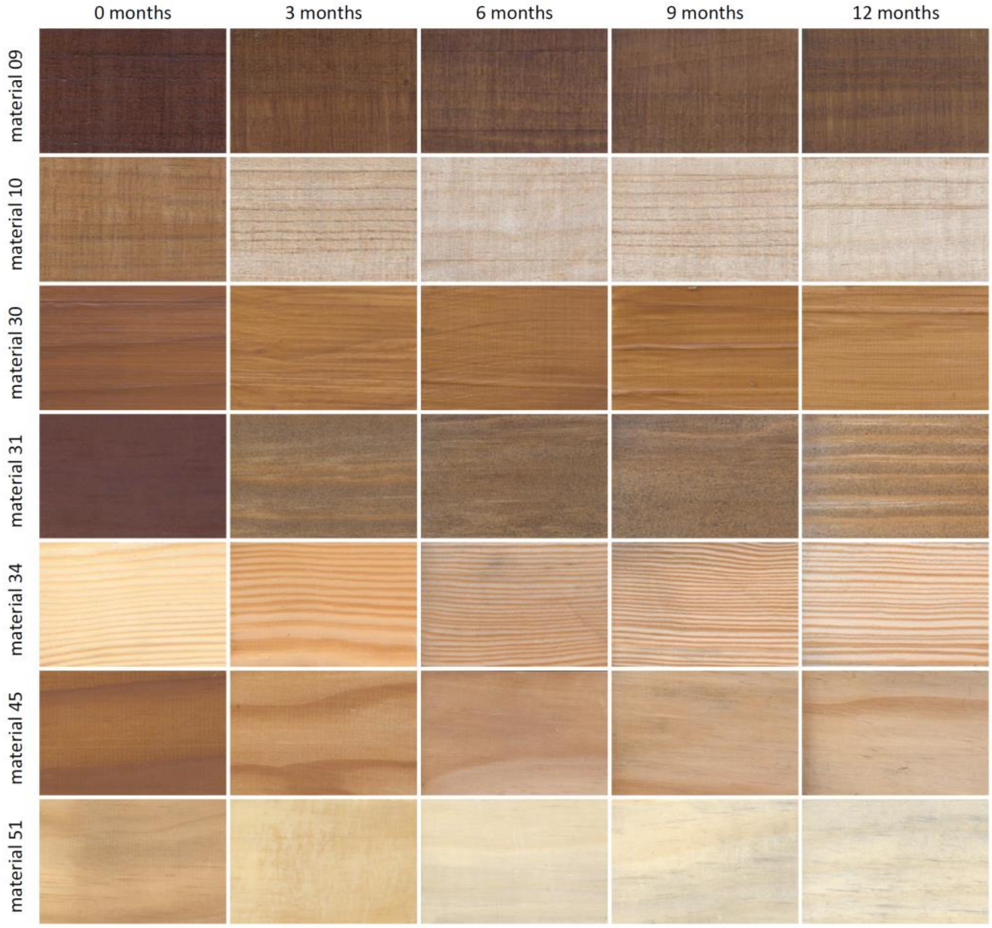

Figure 1: Change of samples appearance due to natural weathering in San Michele all’Adige (Italy)

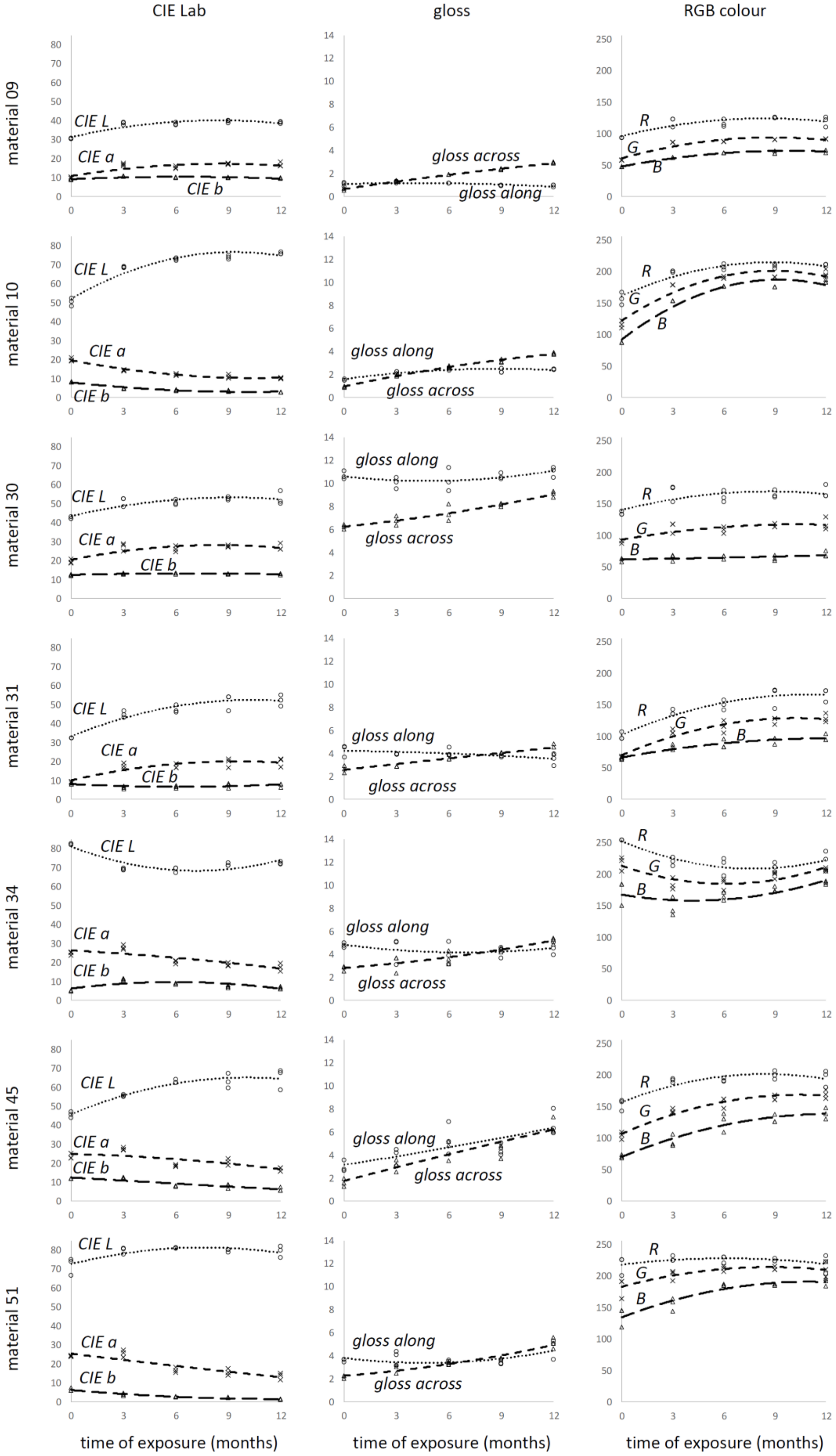

Figure 2: Change of CIE Lab, gloss and RGB parameters due to natural weathering

Chemical changes

NIR spectroscopy was used for non-destructive investigation of chemical composition of samples at different stages of their exposure. However, investigated materials being modified with several modification methods exhibit noticeable differences in their chemical composition already at the initial stage before any weathering. Consequently, differences in appearance of samples and their performance during service life are associated with their chemical composition. Figure 3 present the second derivative of NIR spectra, where functional groups related to key wood components as well as specific futures being results of wood modification are evidenced. The spectra of chemically modified wood (e.g. furfurylated or acetylated) are clearly varying from the other treatments. The highly branched and cross-linked furan polymers are chemically bonded with the wood chemical components as a result of furfurylation (Lande *et al*. 2008). Investigated furfurylated wood (pink spectrum, material #31) possessed spare peak at 6121cm^{-1} (17) not detected in other materials. Acetylation of wood results in a decrease of the number of hydroxyl groups as well as in the increase of the acetyl groups (Schwanninger *et al*. 2011b). In case of acetylated wood (material #51, black line on the Figure 3) shift of several peaks (e.g. 4, 8 or 12) toward higher wavenumbers occurred. Additional peaks 14, 16, 23 and 24, being assigned to CH_3 groups in acetyl ester groups in hemiceluloses, are clearly visible. Likewise, hydroxyl groups detected in the range 6000-7000 cm^{-1} are not evident due to reduction of their number caused by acetylation. Other processes (such as thermal modifications) affected the hemicellulose content, evidenced as a slight reducing of CH functional groups (spectral bands 12 and 13).

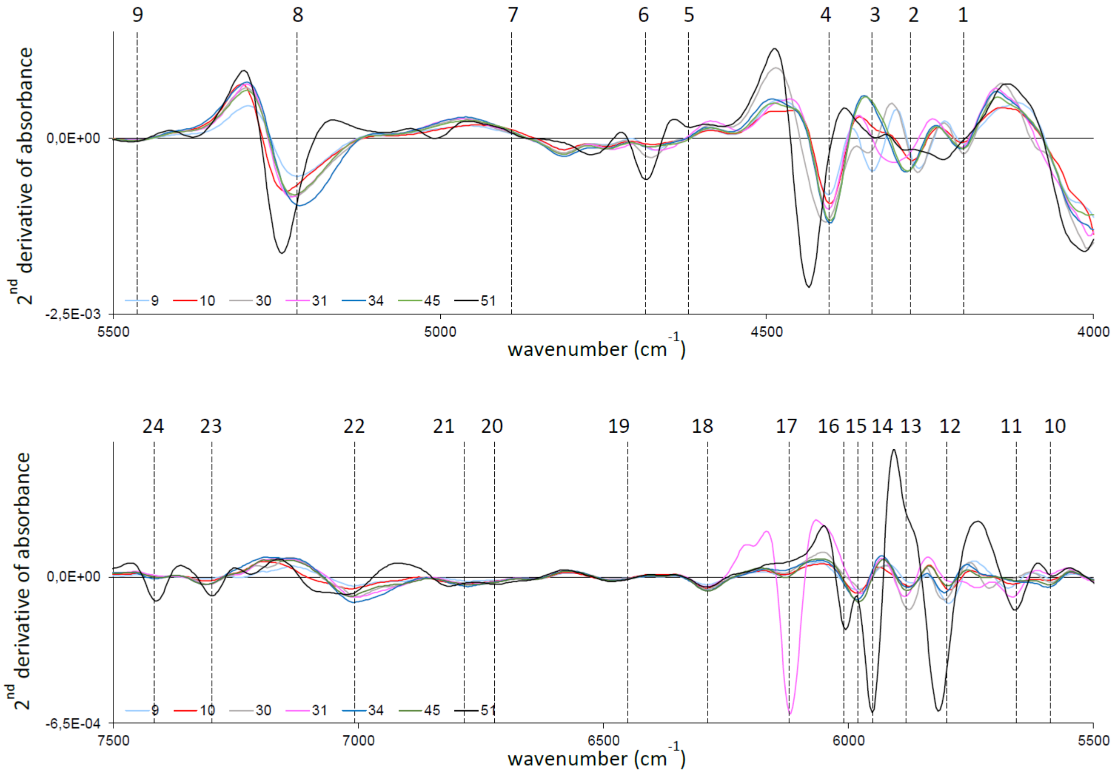

Figure 3: Second derivative of NIR absorbance spectra of investigated materials at their brand new stage

It is expected that natural weathering might affect the chemical composition of materials modified in different processes to various extends. It is due to materials' heterogeneity and variances in their response to the weathering mechanisms. Figure 4 presents a summary of such differences as recorded in the second derivative NIR spectra. In this case, subtraction of reference spectrum from the spectrum of 12 months exposed wood highlights the spectral differences. It is evident that mechanisms of degradation are different for materials after various treatments. Bands 4 and 8 assigned to carbohydrates and water respectively changed in all investigated materials. Even though, the shift of both peaks toward higher wavenumbers is noticed in material #51 (acetylated wood). The presence of positive peak 4 indicates degradation of the functional groups in cellulose and hemicellulose. The reference sample (material #34, pine wood) exhibits the highest changes (positive peaks) for bands: 1, 2, 4 and 8, what indicates decreasing of the functional groups quantity. The distinctive peak 17 observed in furfurylated wood is positive, (as well as bands 1, 3 and 4) what corresponds to the degradation of this component due to weathering. It is important to notice, that functional groups assigned to crystalline and semi-crystalline cellulose (bands: 7, 9, 10, 18, 19 and 20) did not degraded due to weathering in all investigated materials. Cellulose, being more resistant to weathering, became more abundant on the weathered wood surface. According to Kalnins and Feist (1993), the weathering leads to increases of hydroxyl concentration on the wood surface. It is confirmed by slight increase of band 22, assigned to the OH groups in amorphous cellulose. On the contrary, band 15 assigned to functional group of lignin was degraded for all investigated materials, but with different extends. Analysis of the specific degradation kinetics for particular functional groups of wood constituents allow deep understanding of the weathering mechanisms. It highlights week points of investigated materials that might be further improved by optimizing modification processes.

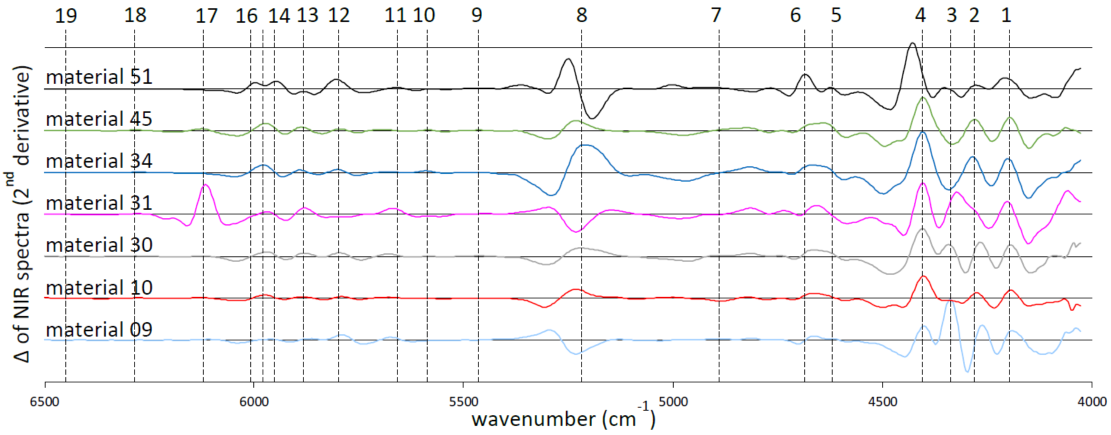

Figure 4: Change in NIR spectra due to 12 months of natural weathering

CONCLUSIONS

The main BIO4ever project output, beside of extensive data base of bio-based materials performance is an interactive software simulating the aesthetic performance of bio-materials integrated with LCA interactive calculation for maintenance operations. At this stage of the software development, all the available data regarding appearance change of each biomaterial in time (CIE Lab, RGB, gloss), weather dose map and specific building layout (UV surface map) are merged together allowing 3D model visualization (Sandak *et al*. 2018a). Time series of pictures that were acquired during exposure of tested materials, presented in Figure 1, are used for the interactive simulation of façades appearance. Software users will be able to choose a material from the database, select the building location and then simulate the structure look at the brand new stage and during its service life (Sandak *et al*. 2018b). The tool, dedicated for investors, architects, construction engineers, professional builders, suppliers and other relevant parties, including also final customers is now under extensive validation and integration with the BIM software.

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Carbon footprint of decking materials – a comparison of modified wood and preservative treated wood

Lars Tellnes[1], Gry Alfredsen[2], Per Otto Flæte[3] and Lone Ross Gobakken[4]

[1]Ostfold Research, Stadion 4, NO-1671 Fredrikstad, Norway. [email: lars@ostfoldforskning.no]
[2]Norwegian Institute of Bioeconomy Research, PO Box 115, NO-1431, Ås Norway.
[email: gry.alfredsen@nibio.no]
[3]Norwegian Institute of Wood Technology, Forskningsveien 3 B, NO-0370 Oslo, Norway.
[email: per.otto.flate@treteknisk.no]
[4]Norwegian Institute of Bioeconomy Research, PO Box 115, NO-1431, Ås Norway.
[email: lone.ross.gobakken@nibio.no]

Keywords: carbon footprint, environmental product declarations, outside decking

ABSTRACT

Carbon footprint over the life cycle is one of the most common environmental performance indicators. In the last years, several wood material producers have published environmental product declarations (EPD) for their products according to EN 15804 which makes it possible to compare the carbon footprint of product alternatives. Comparisons have been performed for different wood cladding intended for use in outdoor facades (Tellnes *et al.* 2014). Outside decks have a different maintenance need and service life than cladding, and a carbon footprint comparison is needed to target this specific application. Reference service lives have been examined for several exterior wood products in Norway (Gobakken *et al.* 2014) and these data has been utilised to make realistic comparisons of wooden decks over the complete life cycle. This paper present and compare the carbon footprint of some of the most common wooden deck materials on the Norwegian market.

INTRODUCTION

Carbon footprint of building materials have had an increased focus as selection criteria when designing buildings and purchasing building products. In the last 10 years, there has been a development of several standards for life cycle assessment (LCA) and environmental product declaration (EPD) for building materials. While LCA is a method to calculate environmental impacts of a product over the life cycle, EPD is a documentation of an LCA for a single product. A EPD for construction products in Europe usually following the EN 15804 and provides data for comparison of products or whole-building LCA. Previous comparisons on claddings has applied data from EPD according to the EN 15804 as a basis for development of the LCA study (Tellnes *et al.* 2014), but some of the materials also needed to be based on other data. Previous LCAs on decking materials have mainly focused on comparing wooden materials to wood-plastic composites (WPC), but the functional unit applied have been different. Bowyer *et al.* (2010) used a functional unit of 100 ft.^{2} of installed decking for a defined service life of 25 years, in which deck boards are 5/4” x 6” solid planks for both solid wood and WPC. Bolin and Smith (2011) used 1000 board feet (30 m^2) per year of use as the functional unit. Furthermore Feifel *et al.* (2015) used a functional unit defined as manufacturing process, 15 year use and disposal of 1 m^2 of a terrace deck consisting of decking boards and sub-construction. The definition of functional unit and service life is regarded as two crucial methodological choices of such studies.

EN 15804 (CEN, 2012) have recently been under revision and prEN 15804 (CEN, 2018) sets out the following criteria for defining the functional units that is the basis for functional equivalent comparison. The requirements relates both to the reference service life (RSL) and how product technical committees (TCs) in standardisation shall develop product category rules for a specific construction product (c-PCR). The requirements are:

a) the application of a product or product groups covered by the functional unit;
b) reference quantity for the functional unit when integrated in the construction works;
c) the quantified key properties, for the functional use or quantified performance characteristics and/or minimum performance of the construction product when integrated into a building, taking into account the functional equivalent of the building;
d) the minimum performance characteristics under defined conditions shall be fulfilled over the defined time period of the functional unit;
e) a specified period of time under reference in-use conditions considering the RSL. If the functional unit uses a different time period than the RSL, the RSL shall be given as technical information in the EPD (see 6.3.3);
f) when developing c-PCR product TCs shall specify the performance characteristics and reference in-use conditions to be included in any functional unit.” (CEN, 2018).

The detailing of the wooden decking installation is crucial and will most often be the factor that determines the service life. The service life can be drastically reduced with unfortunate details. This is shown with the use of ‘worst case’ service life data in Gobakken *et al.* (2014). It is also important to keep in mind that durability is not equal to service life (Brischke *et al.* 2006). Durability is a property that provides a given service life and is affected by a range of factors during the use phase of a product. Service life is a given time period usually specified in years. The service life ends when a property reaches its critical limit of performance. A number of definitions are published regarding the service life of wooden products. The international standard ISO 15686-1 (2011) uses the following definitions:

- Estimated service life (ESL) – “service life that a building or parts of a building would be expected to have in a set of specific in-use conditions, determined from reference service life data after taking into account any differences from the reference in-use conditions”.
- Predicted service life (PSL) – “service life predicted from performance recorded over time in accordance with procedure described in ISO 15686-2 (2012)”.
- Reference service life (RSL) – “service life of a product, component, assembly or system which is known to be expected under a particular set, i.e. a reference set, of in-use conditions and which can form the basis for estimating the service life under other in-use conditions”.
- Design life (DL) – “service life intended by the designer”.

It is crucial to differentiate obsolescence and replacement due to defective performance. According to ISO 15686-1 (2011) “Obsolescence arises when a facility is no longer able to be adapted to satisfy changing requirements”. It is hard to quantify obsolescence since it tends to result from unexpected changes, often unrelated to the construction, but obsolescence will directly influence the service life. Ideally, also obsolescence should be taken into account in an LCA, but since there is a lack of data that determine obsolescence for wood decking this has been omitted in our study

The objective of this study was to investigate the importance of service life aspects to the carbon footprint of decking materials and which can be used in further standardisation of LCA for comparisons of construction products.

METHODS

Goal and scope

The goal of the LCA was to compare the life cycle emissions of modified wood and preservative wood as decking materials. The decking materials included are given below (Table 1).

Table 1: List of deck materials, manufacturers and EPDs included in the study

Product name	Manufacturer	Published	Declaration number	Scope
Thermory pine[a]	Brenstol OÜ	2014	NEPD00259	Cradle-to-grave
Kebony Character pine[b]	Kebony AS	2016	NEPD-410-288	Cradle-to-grave
Accoya Wood[c]	Accsys Technologies	2015	NEPD-376-262	Cradle-to-gate
Copper-impregnated pine in class AB[d]	Moelven Wood AS	2016	NEPD-472-330	Cradle-to-grave
Royal impregnated pine[d]	Moelven Wood AS	2016	NEPD-474-330	Cradle-to-grave

[a]Thermally modified, [b]Furufurylated, [c]Acetylated , [d]Preservative treated

Functional unit

The functional unit of this study was: 1 m^2 of decking manufactured, maintained, replacement necessary for a required service life 30 years and final waste treatment.

Service life and in-situ conditions

The reference service life of wooden decking materials in this study is based on above ground field trials performed in Ås and in Bergen, Norway (e.g. Meyer-Veltrup *et al.* 2017). Based on these data expected service life and 'worst case' service life were estimated and reported in Gobakken *et al.* (2014) for different wood material types. The estimated service life data in Gobakken *et al.* (2014) refer to wood material types and not to specific commercial products. Furthermore, service life data for Royal treated pine was not included in Gobakken *et al.* (2014). For some of the material types a specific estimated service life (ESL) and 'worst case' service lifes (WSL) in years were not specified, only a maximum or minimum range was provided. Based on Gobakken *et al.* (2014) and the latest insight regarding material performance adjusted estimated service life (ESL) and 'worst case' service life (WSL) in years is provided in Table 2. ESL is based on the assumption that best practice is used and WSL is based on the assumption that one or more user errors are performed creating moisture traps resulting in premature decay.

Table 2: List of service life of deck materials. ESL= estimated service life, WSL= worst case service life

Product name	ESL	Adjusted ESL	WSL	Adjusted WSL
Thermory pine[a]	>15	25	<10	9
Kebony Character pine[a]	30	30	<30	20
Accoya Wood	30	35	<30	25
Copper-impregnated pine in class AB[c]	30	30	<30	20
Royal impregnated pine[c]	NA	35	NA	25

[a]Thermally modified, [b]Furufurylated, [b]Acetylated , [d]Preservative treated

Inventory

As the LCA has been performed in the EPD, the main inventory work is the calculation of the results to fit with the functional unit. The material usage of the different decking materials are based on the installation guidelines and all recommend a substructure with 60 cm centre to centre distance of the beams. It is assumed a 5 mm gap between the boards, but the dimensions differ and therefore also the material usage (Table 3). The use of screws and other fasteners are excluded from the study as they were not included in the EPDs.

Table 3: List of deck materials and key number for the inventory

Product name	**Dimensions**	**Length of terrace boards/m2**	**Material use per functional unit [m3/m2]**
Thermory pine[a]	26 x 115	8.33	0.0249
Kebony Character pine[b]	28 x 120	8	0.0269
Accoya Wood[c]	24 x 145	6.67	0.0232
Copper-impregnated pine in class AB[d]	28 x 120	8	0.0269
Royal impregnated pine[d]	28 x 120	8	0.0269

[a]Thermally modified, [b]Furufurylated, [c]Acetylated, [d]Preservative treated

Replacement

How to include different ESL and possible replacements can be very important for the results. Some LCAs take the total life cycle emissions for one product and divide by the number of years ESL. EN 15978 (CEN, 2011) have however another approach based on a required service life of the building and include the number of replacements that is need with the given ESL of the materials. Only a full number of replacements is allowed. Hence, if the number of replacements is calculated to partial amount, the number shall be rounded up. However, if the remaining service life of the building is short in proportion to the ESL of the product, the likelihood of the replacement shall be taken into account. It is assumed here that the function of the decking is crucial for the installation and therefore replaced even in the last year.

Impact assessment

The impact assessment is already performed in the EPDs and global warming potential (GWP) according to EN 15804 are used for the carbon footprint.

Interpretation

In order to understand if the carbon footprint is caused by manufacturing, maintenance, replacement or waste treatment, a contribution analysis has been performed for each material. The contribution analysis is also divided between two approaches to calculate the effect of biogenic carbon on global warming. The first is instantaneous oxidation (GWP–IOBC) where all sequestration of biogenic carbon during forest growth is counted as an emission at harvest. Hence, no emissions of biogenic carbon dioxide is accounted in the rest of the life cycle. The second approach (GWP–total) accounts sequestration and emissions of biogenic carbon at the life cycle module which occurs. The two approaches give the same results over the life cycle under these conditions:

- The wood is from sustainable forestry.
- The wood is utilized through energy recovery without carbon capture and storage at end-of-life.
- The impact assessment does not include time-adjusted characterisation factors.

The required service life of the decking varies between previous studies and are likely to be important for the results. Hence a sensitivity analysis was performed to show how different required service life will change the results.

RESULTS AND DISCUSSION

Comparison

The results of the comparisons of the materials with ESL are given below (Figure 1). The differences are quite large between some of the materials. The thermally modified pine has one replacement in the required service life and this result in a much higher carbon footprint than the other materials. The use of 'worst case' service life increases the difference between some of the materials (Figure 2).

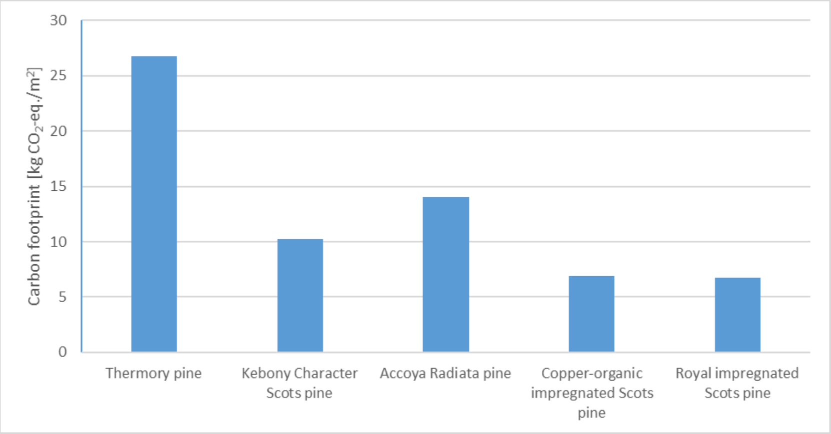

Figure 1: Results of comparison with estimated service life

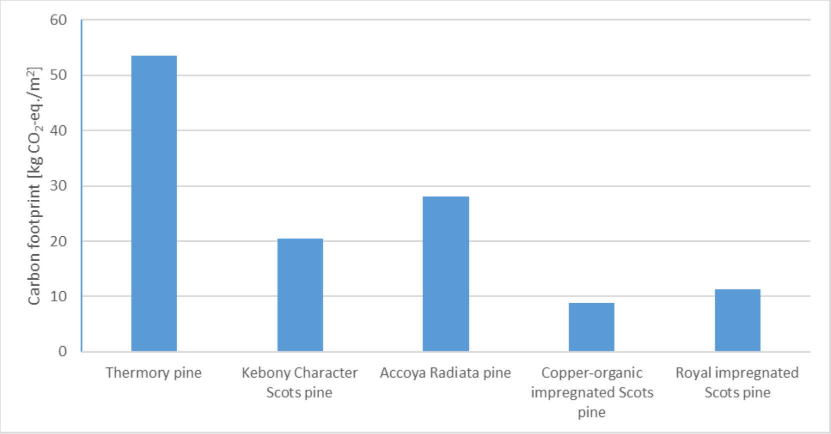

Figure 2: Results of comparison with 'worst case' service life

Contribution analysis

The importance of each life cycle module for the total impact of each material has been assessed through a contribution analysis. The results are given below (Figure 3). The contribution analysis shows that the manufacturing process has a large contribution to the modified wood materials, while the preservative treated also has large contribution from maintenance with oil. In the EPDs, it was assumed added every third year for the Cu-impregnated pine, while it was assumed every 10 years for royal impregnated. For the materials with replacement, this has a large contribution also.

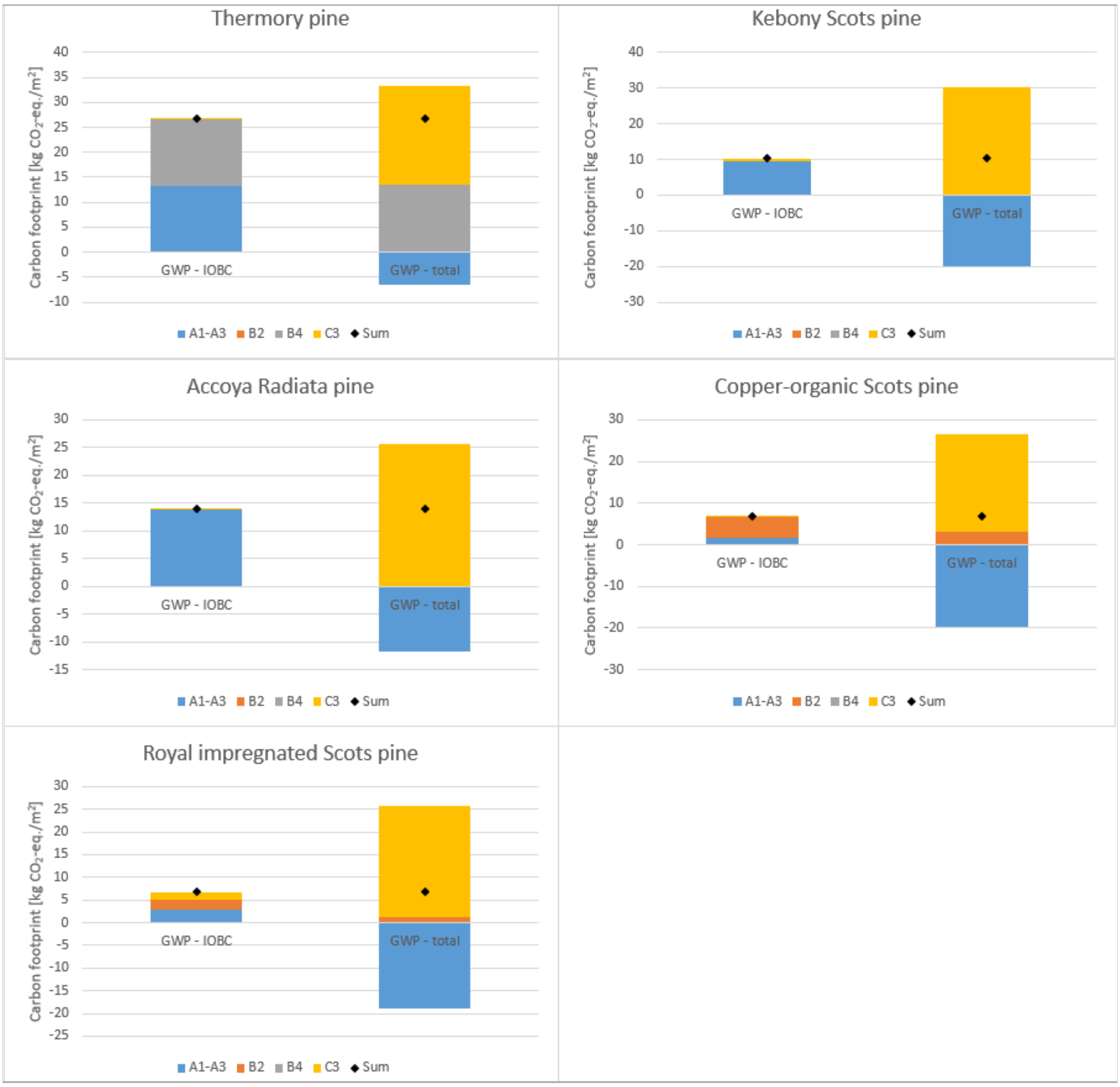

Figure 3: Results of the contribution analysis of each life cycle module A1-A3 = production of the materials, B2 = maintenance, B4 = replacement, C3 = waste treatment.

Sensitivity analysis of required service life

The required service life of the decking may be different from case to case. A sensitivity analysis shows the effect of different required service life on the carbon footprint of the decking materials and the results are given below (Figure 4).

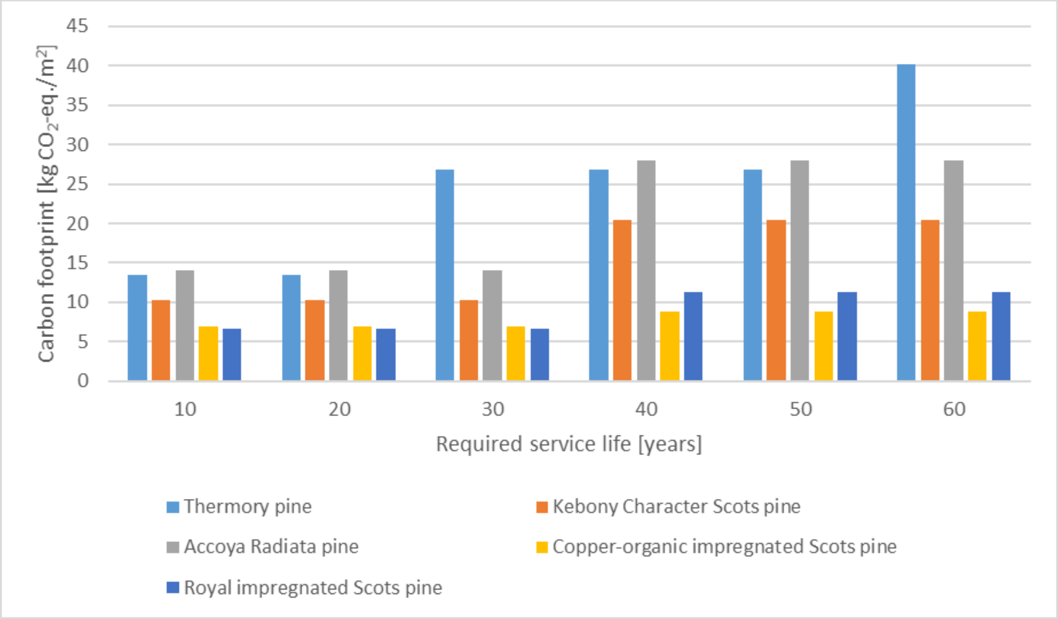

Figure 4: Results of sensitivity analysis with comparison at different amount of required service life

CONCLUSIONS

This study has compared different decking materials based on published EPDs and various service life estimations and requirements. The results show that service life is crucial for the performance raking between some of the products. Decisive issues to be aware of are how the functional unit specifies the functional requirements for the installed product and if full replacement is realistic if there is a short residual life of the installation at the end of the ESL of the material.

For the functional requirements, the weather exposure and requirement for strength performance could be important. For some installation close to ground one could accept breaking of material, but in some that could fatal and replacement would be necessary before breaking is a risk. The different materials also have different dimensions that results in unequal strength properties. In this case all had the same performance requirements, but this could be discussed if is other performance requirements that are relevant. For the materials that need replacement shortly before the end of the required service life, one could discuss that it could be more realistic with a large repair. For instance, replacing 10-50 % of the materials instead of a complete replacement. These two issues should be carefully addressed in developing process of product category rules (PCR) which includes decking materials.

ACKNOWLEDGEMENTS

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SESSION SIX A

Properties 2

Strength classification of acetylated radiata pine

Ferry Bongers[1] and John Alexander[2]

[1]Accsys Group, Westervoortsedijk 73, NL-6827 AV, Arnhem, the Netherlands
[email: ferry.bongers@accsysplc.com]
[2]Accsys Group, 2-19 Lancaster Pl, London WC2E 7EN, UK [email: john.alexander@accsysplc.com]

Keywords: acetylation, mechanical properties, structural design

ABSTRACT

The benefits from acetylation of wood to enhance resistance against fungal decay and dimensional stability have been known for many years. Since 2007 Accsys Technologies has been commercial producing Accoya® wood that is based on acetylation of Radiata pine (*Pinus radiata* D. Don). Accoya® has shown its potential for many applications, including structural uses. Over the years various projects have been realised, and a series of investigations on the mechanical properties of strength graded acetylated radiata pine. A Design Guide for Accoya® structural wood was made on this basis. The research was mostly limited to structural pre-graded radiata pine and to 38 mm thickness. This work presents a detailed investigation of the mechanical properties of (ungraded) acetylated radiata pine ranging from 25 to 100 mm thickness and widths from 100 to 250 mm by Karlsruhe University. In addition initial load duration tests were done. Based on this in combination with quality control processes a strength grade has been allocated to Accoya wood.

INTRODUCTION

The benefits from acetylation of wood to enhance resistance against fungal decay and dimensional stability have been known for many years (Bongers *et al*. 2013, Hill 2006, Rowell and Dickerson 2014). Since 2007 Accsys Technologies has been commercial producing Accoya® wood that is based on acetylation of Radiata pine (*Pinus radiata* D. Don). Accoya® has shown its potential for many applications, including structural uses. Encouraged by the success of the two heavy load-bearing traffic bridges constructed using Accoya® wood in Sneek the Netherlands (Jorissen and Lüning 2010, Tjeerdsma and Bongers 2009), several pedestrian bridges and various other column type structures situated in wet (Service Class 3) conditions have been completed. A design guide for Accoya® structural wood was made on basis of a series of investigations (Bongers *et al*. 2013, 2014). The Karlsruhe Institute of Technology (KIT) in combination and Schaffitzel + Miebach GmbH conducted an extensive study of manufacturing and testing of Accoya Structural Glulam (Blaß *et al.* 2013, Frese and Blaß 2014). This research was based on full size 38 x 150/200 mm beams (both defect free and qualities containing knots) of pre-graded radiata pine.

In 2017 an extensive investigation of the mechanical properties of (ungraded) acetylated radiata pine ranging from 25 to 100 mm thickness and widths from 100 to 250 mm by Karlsruhe University. In addition duration of load tests were conducted. Based on this in combination with quality control processes a strength grade has been allocated to Accoya wood of A1 quality (KIT report 166107, Gutachten Prof. Blaß 2016).

EXPERIMENTAL

Sample preparation

Twenty-six bundles (circa 45m^3) of Radiata pine (Pinus radiata D. Don), from 10 different sawmills from the typical forest areas in New Zealand on both the North and South Island, ranging from 25 to 100 mm thickness and width varying from 100 to 250 mm were allocated for the test. Most boards were of a defect free quality (A1), but (knots) lower visual appearance grade boards (containing either knots, visible resin pockets or wane) were included as a distinct grade (A2 and A3 as defined by Accsys Technologies – Accoya Lumber Grading Specifications). In total 1289 boards were acetylated in the production facilities of Accsys Technologies in Arnhem, the Netherlands, according to the patented process and within the KOMO certification scheme of BRL 0605 (2013). The wood was treated in nine different acetylation batches.

Brookhuis MTG measurements

Prior to and after acetylation the dynamic Modulus of Elasticity was determined with measurements with a Brookhuis MTG by Accsys Group. The method is based on measuring of a frequency response of an impact. The dynamic modulus of elasticity is calculated (Görlacher 1990). For machine grading settings need to be prepared (Ravenshorst *et al*. 2004, Ravenshorst and Van de Kuilen 2014). Of each board prior to acetylation the dimensions, weight and wood moisture content (electric resistance moisture meter) were measured. The Brookhuis MTG was used to determine the natural frequency of the board. The dynamic MOE of each board has been calculated according to Eqn. 1. After acetylation the measurements were repeated except for the wood moisture content (this cannot be measured accurately with a non-destructive device for acetylated wood, but overall the wood moisture content is very low after the process (0 to 3%).

$$MOE_{ViSCAN} = \frac{\rho\left(2L_m f_e\right)^2}{10^6}\ [N/mm^2] \qquad (1)$$

With:

ρ	density in [kg/m3]
L_m	is the board length during the ViSCAN measurements in [m]
f_e	a longitudinal frequency measured by the ViSCAN in [Hz]

Four-point bending tests

A selection of the acetylated wood has been used for 4 point bending tests according to EN 408. The MOR have been corrected for k_h to 150 mm depth in accordance to EN 384. EN 14358 has been used to determine the characteristic bending strength. Most boards have been tested in edgewise position. In addition 25 and 38 mm boards have been loaded flatwise. An overview of the samples is given in Table 1.

Table 1: Test setup of 4 point bending tests

Series	Dimension	Wood quality	Test	# samples
1	25 x 150 mm	A1	Edgewise	30
	25 x 200 mm	A2		20
	25 x 150 mm	A1	Flatwise	31
	25 x 200 mm	A2		20
2	38 x 200 mm	A1	Edgewise	30
	38 x 150 mm	A2		20
	38 x 200 mm	A1	Flatwise	30
	38 x 150 mm	**A2**		21
3	50 x 150 mm	A1	Edgewise	41
		A3		10
4	50 x 250 mm	A1	Edgewise*	40
5	63 x 100 mm	A1	Edgewise	50
		A2		6
6	75 x 100 mm	A1	Edgewise	41
		A2		5
		A3		4
7	100 x 100 mm	A1	Edgewise	50

Shear strength test

Twenty samples Accoya and 20 samples Spruce/Fir have been tested according to EN 408 on shear strength. The Accoya samples have been cut from boards of 38 mm thickness and A1 and A2 quality. Dimensions of the samples is 200 x 80 x 38 mm^3. The samples have been tested with an angle of 14°.

Compression perpendicular to the grain

Forty samples of Accoya were tested according to EN 408 on compression strength perpendicular to the grain. The samples have been cut from Accoya boards of 50, 63, 75 and 100 mm thickness.

Load duration effect testing

From Accoya boards of 25 x 150 mm used for testing of the bending strength (short term testing), 10 boards were cut (lengthwise paired) for testing the effect of load duration. As reference 10 boards of Norway spruce were used. An overview of the properties based upon short term test results is shown in Table 2.

Table 2: Overview of mechanical properties (short term tests). Mean values and standard deviation.

Wood species	N	ρ [kg/m^3]	$E_{dyn\ long}$ [N/mm^2]	$E_{dyn\ bending}$ [N/mm^2]	f_m [N/mm^2]
Accoya	10	500 (18)	8500 (900)	9100 (700)	75.7 (10.4)
Spruce	10	480 (61)	13700 (2000)	14400 (2100)	77.8 (19.1)

The load duration test has been performed according to DIN V ENV 1156. To reduce the amount of load needed the middle part of the board has been reduced to 15 mm height (see Figure 1). Testing has been done at 3 levels; 80, 85 and 90% of the average bending strength determined on short load duration. A load of 40.5 kg has been applied on both ends, the span is variable depending on the load level.

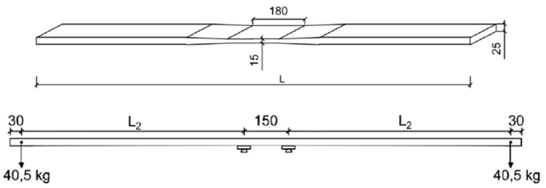

Figure 1: Test set-up – bending under constant load.

RESULTS AND DISCUSSION

Brookhuis MTG measurements

In Figure 2 the dynamic MOE, calculated on basis of the Brookhuis MTG measurement, is shown in relation to the results of the static edgewise bending test for local MOE and MOR respectively. For both A1 and A2 Accoya wood quality the Dynamic MOE has a strong correlation with the local (static) MOE. The correlation with the bending strength (MOR) is less as expected since other factors such as slope of grain play a role.

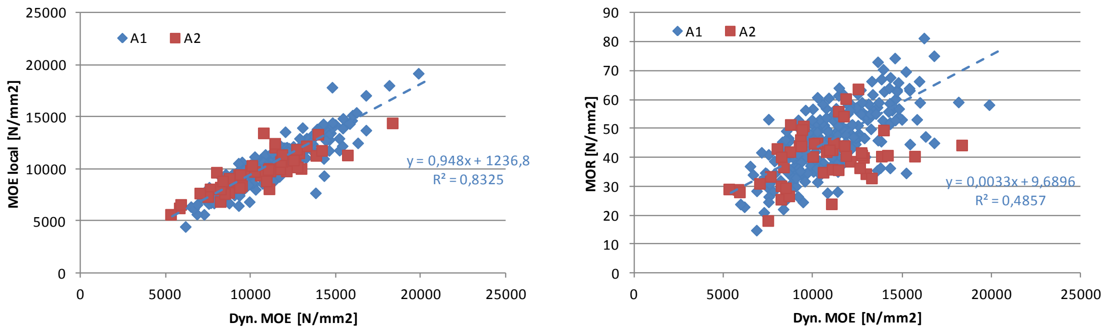

Figure 2: Dynamic MOE in relation to MOE local (left picture) and MOR (right picture) for edgewise bending test

Four-point bending tests

In Figure 3 distributions of the bending strength (MOR) and (local) bending stiffness (MOE) respectively per dimension and wood quality are shown. In total the mean bending strength of 449 boards Accoya radiata pine of different dimensions is 48.7 N/mm^2, and the stiffness 10.000 N/mm^2. The average density is 530 kg/m^3. Influence of the knots on the strength properties could not be found.

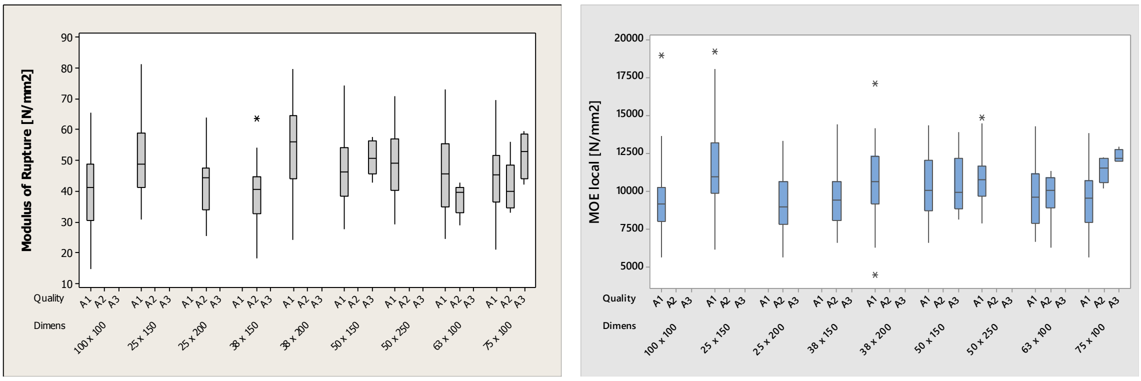

Figure 3: Bending strength distribution (left picture) and Local bending stiffness distribution (right picture) per dimension and quality (edgewise bending tests)

Shear strength tests

The results are summarized in Table 3. Evaluation of the breaking behaviour indicated especially for untreated spruce a brittle behaviour.

Table 3: Results of shear strength test

Series	**N**	***f_m in N/mm²***	
		Mean	**STD**
Accoya RP (A1 quality)*	14	8.3	1.3
Accoya RP (A2 quality)*	6	7.8	1.5
Spruce	20	5.5	1.0

* samples cut from 38 x 150 mm boards

Compression perpendicular to the grain

Table 4 gives a summary of the compression perpendicular to the grain results. Mostly elastic distortions were seen, although some samples had a brittle behaviour.

Table 4: Results of compression strength perpendicular to the grain of Accoya radiata pine.

Series	**N**	***$F_{c,90}$ in N/mm²***	
		Mean	**STD**
3.1 (50x150 mm)	10	10.8	2.2
5.1 (63x100 mm)	10	8.3	0.9
6.1 (75x100 mm)	11	8.7	1.9
7.1 s*) (100x100 mm)	10	8.2	1.2
7.1 l*) (100x100 mm)	10	7.6	1.4

**) s = quarter sawn samples, l = plain sawn samples*

Load duration effect testing

The effect of time on the bending strength is shown in Figure 4. No difference is found between load duration effects for Accoya and spruce. The safety factors (k_{mod} and k_{def}) for softwood described in EN 1995-1-1 may be used for Accoya.

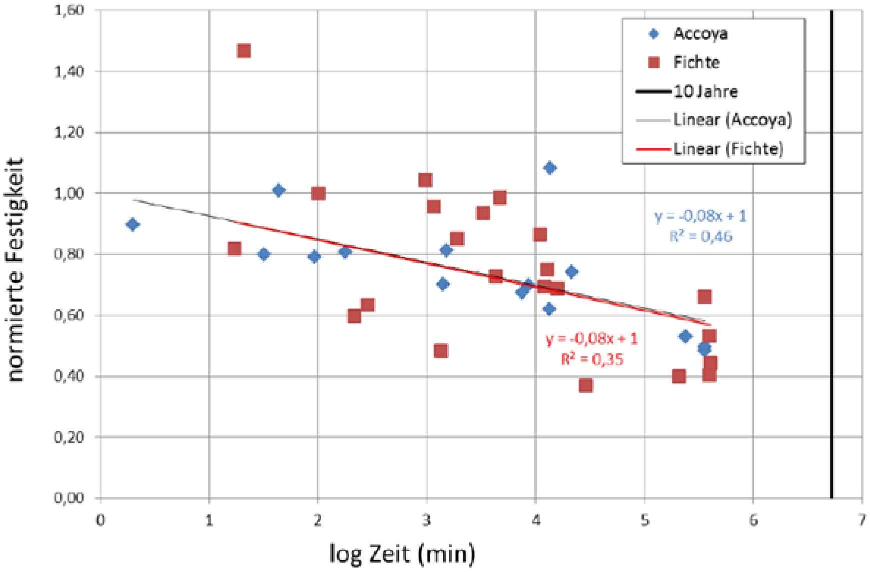

Figure 4: Results of load duration test (time on the x-axis, normalised bending strength on y-axis, Accoya in blue, Norway spruce (=Fichte) in red).

Strength class allocation and other considerations

The characteristic bending strength for the combined wood qualities (A1, A2 and A3) are circa 14% lower than the characteristic value for A1 quality only. A combined grade of A2 and A3 has a circa 26% lower characteristic bending strength compared to A1 quality.

Based upon EN 384 without correction k_h and k_i in combination with the draft EN 14358 (2013) the characteristic bending strength $f_{m,k}$ = 22.7 N/mm^2 for all Accoya qualities combined (A1, A2 and A3). This value is conservative for defect free Accoya (A1) quality since for Accoya containing defects (A2 and A3) the characteristic bending strength $f_{m,k}$ = 16.8 N/mm^2 is used. The characteristic average bending stiffness of Accoya is $E_{0,mean}$ = 9920 N/mm^2, the average density ρ_{mean} = 526 kg/m^3 and the characteristic density ρ_k = 440 kg/m^3. Based on these results it has been proposed by Blaß (2016) to classify Accoya of A1 quality as C22, and Accoya A2 quality as C16 as defined in EN 338. A comparison between the defined C22 class (EN 384) and the test results (combined A1, A2 and A3 quality grades) is given in Table 5.

Table 5: Comparison of values for C22 declared in EN 338 with the research results for Accoya A1.

Property		Value for C22 (EN 338)	Test results
Bending strength	$f_{m,k}$	22 N/mm^2	22.7 N/mm^2
Tensile parallel	$f_{t,0,k}$	13 N/mm^2	17.3 N/mm^2
Tensile perpendicular	$f_{t,90,k}$	0.4 N/mm^2	-
Compression parallel	$f_{c,0,k}$	20 N/mm^2	40.2 N/mm^2
Compression perpendicular	$f_{c,90,k}$	2.4 N/mm^2	4.8 N/mm^2
Shear strength	$f_{v,k}$	3.8 N/mm^2	5.4 N/mm^2
Average stiffness parallel	$E_{0,mean}$	10,000 N/mm^2	9,920 N/mm^2
Stiffness parallel	$E_{0,05}$	6,400 N/mm^2	-
Average stiffness perpendicular	$E_{90,mean}$	320 N/mm^2	-
Average shear strength	G_{mean}	630 N/mm^2	-
Density	ρ_k	340 kg/m^3	440 kg/m^3
Average density	ρ_{mean}	410 kg/m^3	526 kg/m^3

CONCLUSIONS

Based on 4-point bending tests of 449 boards Accoya radiata pine of different dimensions the mean bending strength is 48.7 N/mm^2, and the stiffness 10.000 N/mm^2. The average density is 530 kg/m^3. Influence of the knots on the strength properties could not be determined. The maximum shear strength of the Accoya boards is 8.1 N/mm^2 in average and is higher than found for spruce (average 5.5 N/mm^2). Compression strength perpendicular to the grain gave an average of 8.7 N/mm^2 for Accoya radiate pine.

Based on this and other studies following conclusions and considerations were drawn:

- The standard safety factors as given in EN 1995-1 may be used.
- For the dimensioning of components and connections with pin-shaped connections in Accoya A1, the characteristic strength, stiffness and bulk density characteristics of the strength class C22 should be applied. A comparison between the defined C22 class (EN 384) and the test results (combined A1, A2 and A3 quality grades) is given in the table above. For components made of Accoya A2, those belonging to strength class C16 according to EN 338 should be used.
- Accoya wood connections may be made with nails, clamps, wood screws, dowels and bolts.

- For nails and screws in non-pre-drilled holes, Accoya is considered to be a brittle (splitting sensitive) wood species as defined in EN 1995-1-1 8.3.1.2 (6). In this case, the minimum distances should be maintained as for wood with a characteristic raw density ρ_k of 420 kg/m³ $<\rho_k \leq 500$ kg/m³.

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Effect of DMDHEU modification on physical and mechanical properties of top-layer lamellas for multi-layer parquet flooring

Lukas Emmerich[1] and Holger Militz[2]

[1] University of Goettingen, Wood Biology and Wood Products, Faculty of Forest Sciences, Buesgenweg 4, D-37077 Goettingen, Germany [lukas.emmerich@uni-goettingen.de]

[2] University of Goettingen, Wood Biology and Wood Products, Faculty of Forest Sciences, Buesgenweg 4, D-37077 Goettingen, Germany [holger.militz@uni-goettingen.de]

Keywords: Brinell hardness, dimensional stability, DMDHEU, dynamic hardness, flooring, testing

ABSTRACT

Wood modification with 1.3-dimethylol-4.5-dihydroxyethyleneurea (DMDHEU) was studied intensively since the late 1990s. Originally, this modification technology has been transferred from textile to wood application, with a focus on the treatment of permeable Scots pine sapwood (*Pinus sylvestris* L.). Results of various studies on DMDHEU wood modification have been summarized recently by Emmerich *et al.* (2017). The main benefits provided by this treatment of wood were shown to be an improved dimensional stability, biological durability and an increase in surface hardness. Within this study, DMDHEU wood modification was transferred to 'new' wood species, namely Rubberwood (*Hevea brasiliensis* Müll. Arg.) and English oak (*Quercus robur* L.). Since the latter are less permeable than Scots pine sapwood, the approach was to treat thin and rough sawn top-layer lamellas that could later be glued on a carrier plate to produce multi-layer parquet flooring. The objectives of such treatment were to improve the dimensional stability and surface hardness of the final product. Swell rates were reduced by treatment with DMDHEU. Compared to untreated control samples, modified English oak showed an *ASE* of 45 - 50 %. For Rubberwood, the *ASE* was minor at approx. 25 % and in contrast to English oak no additional increase in *ASE* detected at higher treatment level. Brinell hardness (EN 1534 2011) and dynamic hardness were tested using two different experimental setups. The surface hardness increased by DMDHEU treatment and with rising treatment level for both, Rubberwood and English oak. This was confirmed both within static and dynamic testing and a correlation detected between static and dynamic hardness. Nitrogen analysis was conducted in order to evaluate the uniformity of DMDHEU loadings along impregnated lamellas, cured in a pilot scale drying plant. The variation in DMDHEU loadings along the lamellas and between earlywood and latewood was higher in DMDHEU treated English oak compared to Rubberwood which may explain higher variations of surface hardness and further properties in English oak.

INTRODUCTION

Parquet flooring is expected to have a high dimensional stability under changing climate conditions and an adequate surface hardness. From an aesthetic perspective, a surface finish as well as cleaning and care should be easy to make. With increasing wear on the flooring (e.g. hotels, office buildings) the requirements for respective properties increase continuously. The latter can be solved either by choosing suitable wood species, mainly tropical hardwood species that originally show the respective property profile, or by wood modification technologies that may enhance the required characteristics. Modification candidate technology to increase both dimensional stability and hardness is the treatment with 1.3-dimethylol-4.5-dihydroxyethyleneurea (Figure 1, Krause 2006).

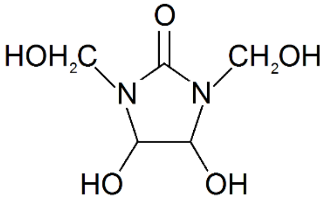

Figure 1: Structural formula of 1.3-dimethylol-4.5-dihydroxyethyleneurea (DMDHEU, Schindler and Hauser 2004, adapted).

Incorporated in wood within a water-based solution by a vacuum-pressure impregnation process and finally cured at temperatures of approx. 120 °C, DMDHEU monomers were shown to penetrate wood cell walls by a permanent cell wall *bulking*. The latter depends upon the concentration of DMDHEU and the selected catalyst (Krause *et al.* 2003). Since a uniform solution uptake constitutes the basic requirement for a successful modification of large-size timber boards, previous investigations focused on permeable Scots pine sapwood (*Pinus sylvestris* L.) and to some extent on European beech (*Fagus sylvatica* L., Krause 2006, Bollmus 2011). For Scots pine a process was developed up to pilot scale (Schaffert 2006).

The overall aim of this study was to transfer the treatment with DMDHEU to ‘new’ wood species. In particular, English oak (*Quercus robur* L.) was tested as a wood species with a long tradition for parquet flooring in parallel with Rubberwood (*Hevea brasiliensis* Müll. Arg.) that in untreated state shows lower hardness but higher permeability compared to English oak (Wagenführ and Scheiber 2007). Thus, mainly the latter was considered to be promising for a treatment with DMDHEU and characteristic’s improvement on a ‘high level’. Especially English oak is less permeable compared to Scots pine sapwood (EN 350 2016), what would affect a full core impregnation. Thus, the approach was to treat thin (approx. 4 mm) and rough sawn lamellas that could later be glued on a carrier plate to produce multi-layer parquet flooring with improved characteristics, mainly dimensional stability and surface hardness.

EXPERIMENTAL

Wood and chemicals

Rubberwood (*Hevea brasiliensis* Müll. Arg.) and English oak (*Quercus robur* L.) specimens were treated with the cross-linking agent 1.3-dimethylol-4.5-dihydroxyethyleneurea (DMDHEU). A solid content of approx. 67 % w/w of the DMDHEU stock solution was determined following EN ISO 3251 (2008). Wood specimens were treated at two treatment levels by adding 30 % or 50 % of the DMDHEU stock solution to a water-based impregnation solution. As catalyst magnesium nitrate hexahydrate ($Mg(NO_3)_2 \times 6\,H_2O$) was added in a concentration of 2 % related to the added DMDHEU stock solution. Wood specimens were either 15 x 15 x 10 (ax.) mm^3 or rough sawn lamellas (‘rift cut’) of 4 x 35 x 900 (ax.) mm^3. The latter were glued as top-layer lamellas on a carrier plate (plywood, 18 mm thickness) to produce multi-layer parquet flooring elements for surface hardness testing.

Treatment

Two different treatment processes were applied. After a vacuum-pressure impregnation (-0.98 bar (1 h); 12 bars (2 h)) wood specimens were dried at room climate for 120 h and afterwards cured at 120 °C for 48 h (15 x 15 x 10 (ax.) mm³) or 24 h after a stepwise temperature increase from 60 °C to 120 °C (4 x 135 x 900 (ax.) mm³). Solution uptake, weight percent gain (*WPG*), dimensional stability and surface hardness were tested after treatment.

The second process was a superheated steam process, following the upscaled process for Scots pine. After impregnation, lamellas of 4 x 135 x 900 (ax.) mm³ were placed in a pilot plant kiln and the DMDHEU reacted with superheated steam at 120 °C. Respective specimens were used to determine the modification quality on the basis of a homogeneous DMDHEU distribution that finally determines a uniform material performance. For this, samples were cut 100 mm from each end of the lamellas and subjected to a nitrogen analysis.

Bonding

Untreated and modified lamellas for hardness testing were glued on a carrier plate (18 mm plywood) with a PVAc glue (‘Ponal Super 3’, D3, Henkel AG & Co. KGaA) applying the following press parameters: pressing pressure: 0.7 N/mm²; press temperature: 25 °C; press duration: 16 h.

Chemical loading and quality control

Oven-dry weights and cross-sectional dimensions before (M_1, A_1) and after treatment (M_2, A_2) were determined. W*eight percent gain* (Eqn. 1) and cell wall *bulking* (Eqn. 2) were determined.

$$WPG\ (\%) = ((M_2 - M_1)/M_1) \times 100 \qquad (1)$$

$$Bulking\ [\%] = ((A_2 - A_1)/A_1) \times 100 \qquad (2)$$

Specimens subjected to a nitrogen analysis (Kjeldahl method in a FoodALYT system by OMNILAB Bremen, Germany: Block digestion system SBS 850, steam distillation D 1000 and back titration TS 10) were taken at different locations along the lamellas treated within the steam process and milled in a cutting mill with a mesh size of 2 mm. The nitrogen content [%] was determined and related to the oven dry mass of wood samples. Sample locations were compared in regards to the absolute nitrogen content and thus homogeneity of the treatment within single lamellas evaluated. For English oak nitrogen content was determined separately for earlywood and latewood areas.

Dimensional stability

Dimensional stability was tested and quantified by the Anti Swell Efficiency (*ASE*) according to Hill and Jones (1996) over 3 cycles of water saturation (two-dimensional swelling coefficient [%]) and re-drying to 0 % moisture content (*MC*). The dimensions of tested wood specimens were 15 x 15 x 10 (ax.) mm³ and changed between oven dry (d) and water saturated state (w). Ten replicates of each wood species and treatment level were tested and the *ASE* calculated (Eqn. 3).

$$ASE\ [\%] = ((S_c - S_m)/S_c) \times 100 \qquad S\ [\%] = ((A_w - A_d)/A_d) \times 100 \qquad (3)$$

Hardness

Five lamellas per wood species and treatment level were selected and glued on a plywood carrier plate, untreated controls included. From each lamella of 4 x 135 x 900 (ax.) mm³ three specimens of 110 (ax.) x 110 x 22 mm³ (lamella plus plywood carrier plate) were cut at different positions and used for hardness testing. Prior to testing, all specimens were conditioned at 20 °C and 65 % RH.

Brinell hardness test

The Brinell hardness [N mm^{-2}] was determined according to EN 1534 (2011) with a universal testing machine Zwick 10 kN (ZWICK GmbH und Co. KG). A steel ball (10 mm diameter) was pushed into the wood with 1000 N for 30 s and the diameters of the indentations were measured to calculate the Brinell hardness [N mm^{-2}]. The Brinell hardness test was conducted at five measurement points on each of fifteen replicates per wood species and DMDHEU treatment level.

Dynamic hardness

Two different dynamic experimental setups were used to determine the surface hardness of DMDHEU modified multilayer parquet flooring. The specimens were the same as used for the Brinell hardness test. First an ‘Impact tester’ in the form of a stainless steel bolt with a rounded, spheric tip and a weight of 1000 g was dropped on the wooden surface from 1 m height (‘free fall‘). The maximum depth of indentation [mm] was measured with a dial indicator (Mitutoyo Corporation, Kawasaki, Japan) at four measurement points per specimen.
A second test method and device were described by Meyer *et al.* (2011). A steel weight of 500 g fell down (‘free fall‘) from a height of 0.3 m on a steel ball (10 mm diameter). A carbon paper between steel ball and wood surface made the indentation visible so that the diameters were measured crosswise and the radius [mm] of the indentation was calculated. The dynamic hardness was calculated in terms of the momentum/indentation area (Eqn. 4) where m is the mass of the drop weight [kg], h is the dropping height [m], r is the radius of the indentation [mm] and g is the gravitational acceleration [m s^{-1}]. The number of measurement points was two per specimen.

$$HD\ [kg\ m^{-1}\ s^{-1}] = p/A = ((m \times (2 \times g \times h)^{0.5}) / (\pi \times r^2)) \times 1\ 000\ 000 \qquad (4)$$

For each replicate mean values were calculated and a correlation between Brinell hardness and both dynamic hardness parameters investigated.

RESULTS AND DISCUSSION

Weight gains, cell wall bulking, swelling and shrinking properties (dimensional stability) and surface hardness were tested with DMDHEU impregnated specimens that had been cured at 120 °C in drying ovens under dry conditions. After material characteristics were shown to be improved significantly by DMDHEU treatment, impregnated lamellas were subjected to a superheated steam process in order to reduce drying failures (cracking, deformations) that had been observed after a ‘dry curing’.

Treatment – Weight gain and bulking

Rough sawn lamellas were impregnated at an initial *MC* of 4.85 (± 0.48) % (Rubberwood) and 6.72 (± 0.35) % (English oak). Solution uptakes calculated were at 102 – 141 % (Rubberwood) and 26 – 83 % (English oak) and indicated a minor permeability of English oak compared to Rubberwood. Depending on the solution uptake, the absolute *WPG* increased with increasing chemical concentration and was higher for Rubberwood compared to English oak (Figure 2, a). *Vice versa*, higher cell wall penetration of DMDHEU monomers was detected by a permanent *cell wall bulking* of English oak, although *WPG* levels were below the ones of Rubberwood (Figure 2, b). Thus, higher amounts of DMDHEU seemed to be located within the cell lumen of Rubberwood samples in comparison with English oak.

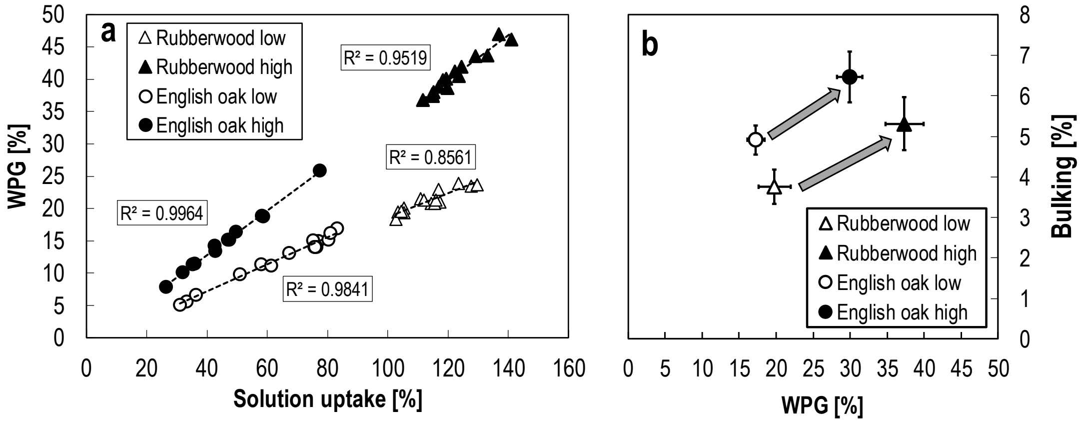

Figure 2: Treatment process – Weight percent gain (WPG) depending on solution uptake (a) and cell wall bulking depending on WPG (b) separately for various treatment levels and wood species

Dimensional stability

The *ASE* was determined over three cycles of water saturation and re-drying. Modified English oak revealed an *ASE* of 45 % (low treatment level) and 50 % (high treatment level) at the end of three ‘swell-and-shrink’ cycles. For Rubberwood, the *ASE* was minor (25 %) and no significant increase detected at higher treatment level (Figure 3, b).

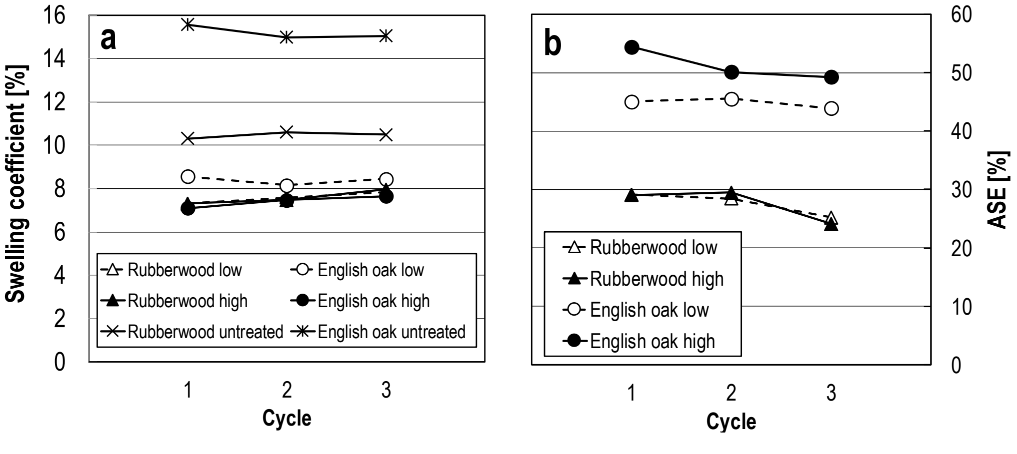

Figure 3: Absolute swelling coefficients (a) and Anti swell efficiency (b) of Rubberwood and English oak treated with various DMDHEU concentrations

However, absolute swelling coefficients [%] were similar after treatment for both Rubberwood and English oak. Minor *ASE* values calculated for Rubberwood, were therefore affected by minor moisture-induced swelling of untreated Rubberwood compared to English oak (Figure 3, a).

Hardness

The Brinell hardness of the modified lamellas increased with increasing DMDHEU treatment level independent of the wood species (Figure 4). Earlier studies by Krause (2006) and Bollmus (2011) confirmed this effect of DMDHEU treatment for Scots pine and European beech wood. Regarding the relative hardness increase caused by DMDHEU treatment, a modification with

DMDHEU was more effective in Rubberwood. Accordingly, the impregnation and uptakes proved to be decisive for the final treatment success and material performance (Krause 2006). The dynamic hardness of both wood species was increased by DMDHEU treatment as well and a correlation between Brinell hardness and dynamic hardness found, illustrated for Rubberwood in Figure 4. These findings confirmed results of *Meyer et al.* (2011) so that dynamic hardness increased with increasing Brinell hardness even if the correlation detected was minor in case of modified English oak. Depth of indentation measured after ‘impact testing’ decreased with increasing Brinell hardness for both Rubberwood and English oak. At a certain Brinell hardness level both dynamic hardness parameters seemed to reach a saturation point (Figure 4, a, b).

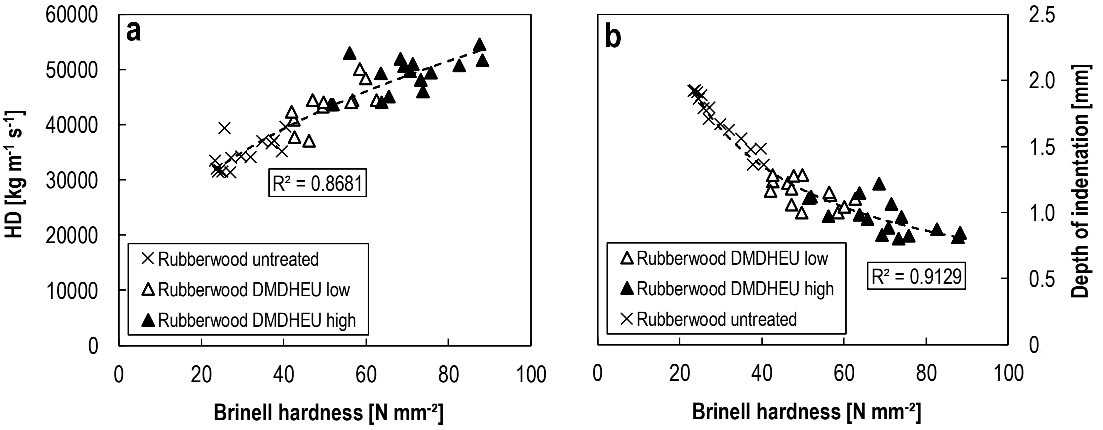

Figure 4: Relationship between dynamic hardness HD and Brinell hardness (a) and relationship between depth of indentation (‘impact tester’) and Brinell hardness (b) for Rubberwood (a, b)

Figure 5 illustrates the Brinell hardness and dynamic hardness *HD* depending on the treatment level (*WPG*).

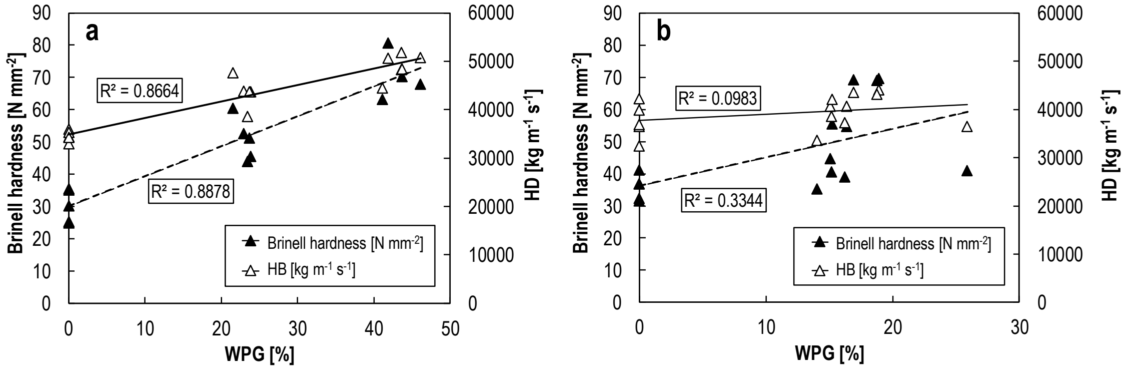

Figure 5: Brinell hardness and dynamic hardness HD depending on WPG separately for Rubberwood (a) and English oak (b)

For Rubberwood a strong correlation between both hardness parameters was found by hardness values that increased with increasing *WPG* (Figure 5, a). For English oak this correlation was less obvious, regarding *WPG* levels and mean hardness values of single lamellas (Figure 5, b). The latter indicates that in modified English oak samples higher variations in regards to the DMDHEU distribution might be present that finally effect a uniform material performance (e.g. hardness, dimensional stability). Depending on the annual ring orientation within the sawn lamellas, also the textural structure of English oak (ring porous wood) might effect such variations concerning the material performance.

Quality control - Nitrogen content and nitrogen distribution

DMDHEU impregnated lamellas (4 x 135 x 900 (ax.) mm³) were dried and cured within a superheated steam process. Regarding the total lamella, with increasing *WPG* levels, the nitrogen content increased. Both parameters showed a strong linear correlation and thus do equally suit for the assessment of total DMDHEU treatment level expressed by the chemical loading (Figure 6, a). In contrast to the nitrogen content determination, *WPG* calculation does inevitable require the knowledge about the oven-dry weight of the specimens before and after treatment and thus is not appropriate for industrial applications. Finally, nitrogen analysis was required to evaluate the uniformity or differences in chemical loadings within treated lamellas. In summary, absolute nitrogen contents within modified English oak boards varied between 0.37 - 0.52 %, along treated Rubberwood lamellas between 0.37 – 0.58 %. Related to the total nitrogen contents (relative value), DMDHEU distribution was more uniform within Rubberwood compared to English oak. The separate analysis of English oak earlywood and latewood areas revealed significantly reduced DMDHEU loadings within the latewood whereby respective differences enlarged with increasing treatment level (Figure 6, b). Both aspects may provide an explanation for higher variations detected within surface hardness testing of treated English oak samples.

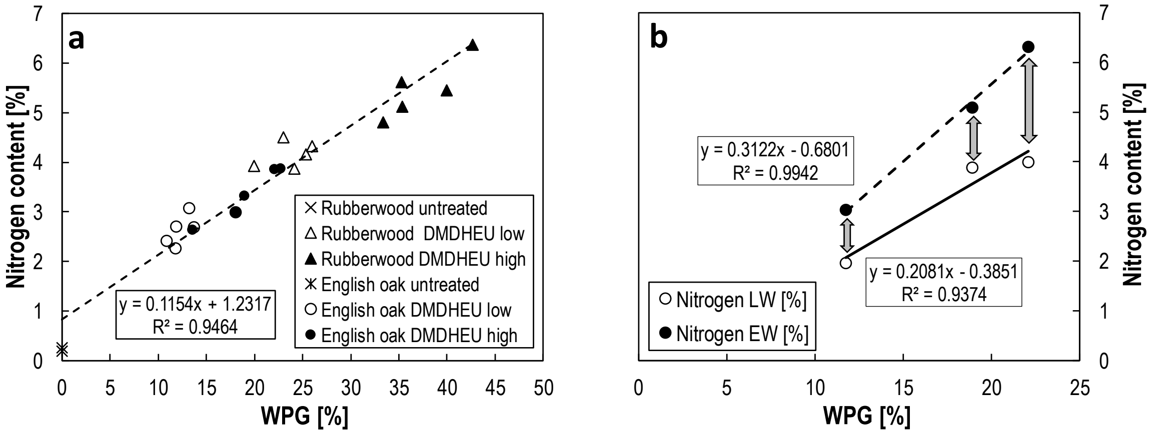

Figure 6: Relationship between nitrogen content and WPG depending on wood species and treatment level (a) and separated for earlywood (EW) and latewood (LW) in case of English oak (b)

CONCLUSIONS

In summary, DMDHEU treatment was shown to improve material characteristics relevant for parquet flooring for both Rubberwood and English oak, treated in the form of thin solid wood lamellas. Depending on the product requirements that are for parquet flooring mainly surface hardness and dimensional stability, the degree of characteristic's improvements was shown to be easily controlled by the chemical concentration within a water-based impregnation solution. In comparison of Rubberwood and English oak, the latter showed slightly increased variations in DMDHEU distribution within treated lamellas and between earlywood and latewood areas but in a range that is not decisive and critical for a homogeneous product performance. Future investigations will focus on the further processing of the modified material, required for multi-layer parquet flooring production, in particular adhesives and coating application.

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Cutting forces when machining thermally modified poplar – preliminary results

Giacomo Goli[1], Rémi Curti[2], Bertrand Marcon[2], Antonio Scippa[3], Marco Fioravanti[1], Gianni Campatelli[3], Louis Denaud[2]

[1]GESAAF - University of Florence, Via S. Bonaventura 13, IT-50145, Florence [email: giacomo.goli@unifi.it – marco.fioravanti@unifi.it]
[2]LaBoMaP – Arts et Métiers Paristech, Rue porte de Paris, FR-71250 Cluny [email: remi.curti@ensam.eu, bertrand.marcon@ensam.eu, louis.denaud@ensam.eu]
[3] DIEF - University of Florence, Via Santa Marta 3, IT-50139, Florence [email: antonio.scippa@unifi.it – gianni.campatelli@unifi.it]

Keywords: cutting forces, grain orientation, poplar wood, thermal modification

ABSTRACT

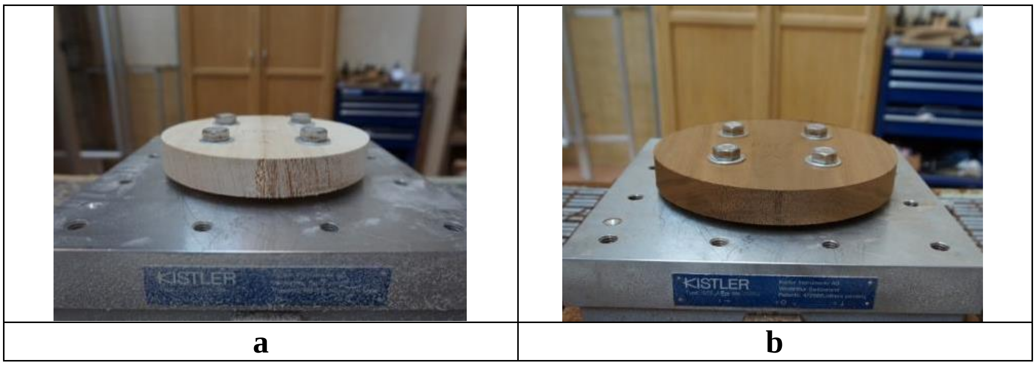
This work explores the possibility, with a simple and innovative procedure, to assess the machining properties of thermally modified wood for a whole set of grain orientations and compare the results with unmodified wood. An experimental test set up was designed, few exploratory tests performed and a data analysis procedure developed. This method has shown to work fine to describe and compare the cutting forces of unmodified and thermally modified wood at different grains orientations. With a simple test a whole set of grain orientations can be acquired and with few tests performed at different depths of cut it is possible to evaluate the specific cutting forces. The forces when machining unmodified and thermally modified wood have shown to be very similar when machining along the grain. However, the cutting forces when machining thermally modified wood with or against the grain have shown to be lower than for untreated wood. The data analysis method, actually based on filtering the signals that are strongly affected by the system dynamical excitation, should be improved in order to calculate the real cutting forces acting.

INTRODUCTION

The use of thermally modified wood is getting more and more frequent in different uses such as: internal furniture for its dark colour, in use in wet conditions, external use where durability and hygroscopic stability are needed. It is also getting easier and easier to find this product on the market. Even if thermally modified wood is not a new product, the efforts of researchers until now have been focused mainly on treatment processes, chemical analysis, durability, dimensional stability, and mechanical performances. The machining of modified wood is something not very explored yet. Some information about handling, machining and gluing of this material can be found on (Finnish ThermoWood Association 2003). The quality after machining has also been assessed by different authors such as (de Moura *et al.* 2011; Budakçı *et al.* 2013; de Moura Palermo *et al.* 2014; Tu *et al.* 2014; Palermo Pires De Moura *et al.* 2015; Sandak *et al.* 2017). The cutting forces as well as the specific cutting coefficients are not investigated yet. In this article, the general approach described in (Goli and Sandak 2016) was used for the machining of unmodified and thermally modified poplar wood disks. The same disk (one for thermally modified wood and one for unmodified wood) was machined with different depths of cut (0.3, 0.7, 1.1, 1.5 mm) and the forces measured on two horizontal orthogonal directions (X, Y) in order to assess the cutting forces when machining with different depths of cut and grain orientations. This work is not meant to give extensive information on cutting forces and to precisely assess the specific cutting coefficients; but the aim is to explore the possibility to assess the machining properties of thermally modified wood at a whole set of grain orientation, compared to unmodified wood using an innovative and rapid procedure.

EXPERIMENTAL

Two boards of unmodified and thermally modified poplar wood (*Populus* sp.) were machined into a disk shape. Afterward, the disk was stiffly screwed on a Kistler 9255 type tri-axial piezoelectric dynamometric platform for the measurement of the cutting forces. The platform was driven by a Kistler type 5019 charge amplifier set with 100 $N.V^{-1}$ and "Long" time constant mode. The tests on the disks were done with a low-pass filter with a cut-off frequency of 10 kHz in order to avoid aliasing. The disk was machined using a SCM Record 1 3-axis CNC centre. The machining was done by a single straight blade balanced tool in order to get an invariant chip thickness.

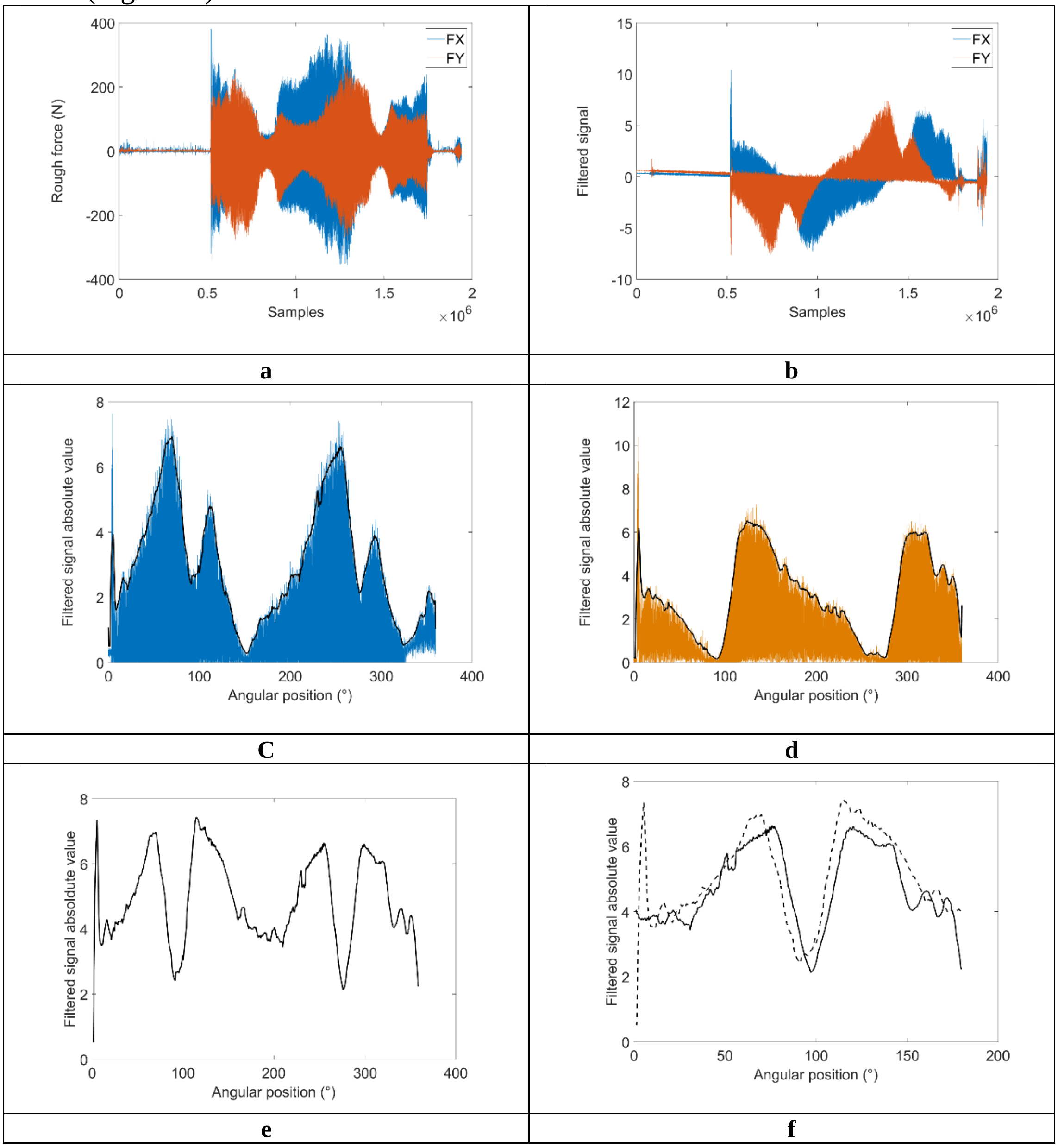


a b

Figure 1: Experimental set up of the wood disks screwed on the dynamometric platform. a) untreated poplar and b)thermally modified poplar.

The diameter of the tool was 80 mm and the blade was a tungsten carbide freshly sharpened insert with a rake angle of 25° and a blade angle of 55°. The spindle was set to rotate at 3000 rpm both for measurement and preparatory cut. For every depth of cut the surface was prepared before the measurement by machining 0.2 mm of depth of cut in 5 successive steps with a feeding speed of 1 $m.min^{-1}$. The measurement of the cutting forces was done after surface preparation, machining with up-milling technique and with a feeding speed of 3 $m.min^{-1}$. The analogue outputs of the charge amplifiers were acquired synchronously with a sampling frequency of 50 kHz by a 16 bits National Instrument acquisition board model NI-9215 installed on a USB chassis model cDAQ-9174. The different channels were acquired by DASYLab® software and analysed with MATLAB®. Wood was machined after a stabilizing period in internal environment with a moisture content of 7.8% for untreated one and 6.4% for thermally modified one. The density at standard environmental conditions (20 °C @ 65% relative humidity) was determined to be 330 $kg.m^{-3}$ and 340 $kg.m^{-3}$for for untreated and thermally modified wood respectively. Thermally modified poplar was treated at 215 °C using the ThermoWood® process. The rough signals obtained machining a disk are shown in Figure 2a for X- and Y-axis. As can be seen the noise, depending on the dynamic excitation of the system, is very high and the vibration of the machine does not allow to separate positive and negative forces. The cut in milling with one blade is highly discontinuous explaining why the whole system (wood disk + dynamometer + machine environment) is strongly solicited dynamically to vibrate at its natural frequency (about 1.5 kHz). In order to verify that the rough force could include relevant information of the acting process, the signals were low-pass filtered with a cutting frequency of 200 Hz. The result of the filtering is shown in Figure 2b. As it can be observed, a large part of the free vibration is removed. The values of forces obtained with this procedure were then plotted as absolute values versus the angular position for the X-axis (Figure

2c) and for the Y-axis (Figure 2d) and the envelope extracted through a Matlab® code. Both graphs present two symmetric parts corresponding to first and second half of the disk. The X- and Y-axis envelope values were then used to calculate the resulting force as sum of vectors, as reported in Figure 2e. Because the disk is made of two equal halves (axially symmetric regarding the grain orientation), the resulting force was computed as the average of these two halves (Figure 2f).



a

b

C

d

e

f

Figure 2: These graphs are obtained by processing the test performed on thermally modified poplar wood machining with a depth of cut of 1.1 mm. a) Rough forces vs number of samples, b) 200 Hz low-pass filtered cutting forces vs. number of samples, c) Force on the X-axis with its envelope vs the angular position, d) Force on the Y-axis and its envelope vs. angular position, e) Resulting force calculated as vectors sum of X- and Y-axis components vs. angular position, and f) Resulting force is divided in two halves corresponding to half disks and the two halves averaged.

To summarize, this simple data processing doesn't allowed to obtain the true values of cutting forces, but at least to make a first assessment of the possibility to make comparisons unmodified and thermally modified wood. The same procedure could ba applied to different materials, using different tools etc.

RESULTS AND DISCUSSION

The data obtained applying the above presented method when machining unmodified and thermally modified wood are shown in Figure 3. The continuous line indicates unmodified wood while dashed line indicates thermally modified wood. In blue are shown the cutting forces when machining at 0.3 mm of depth of cut (*DOC*), in red when machining with 0.7 mm DOC, and in orange when machining with 1.1 mm DOC.

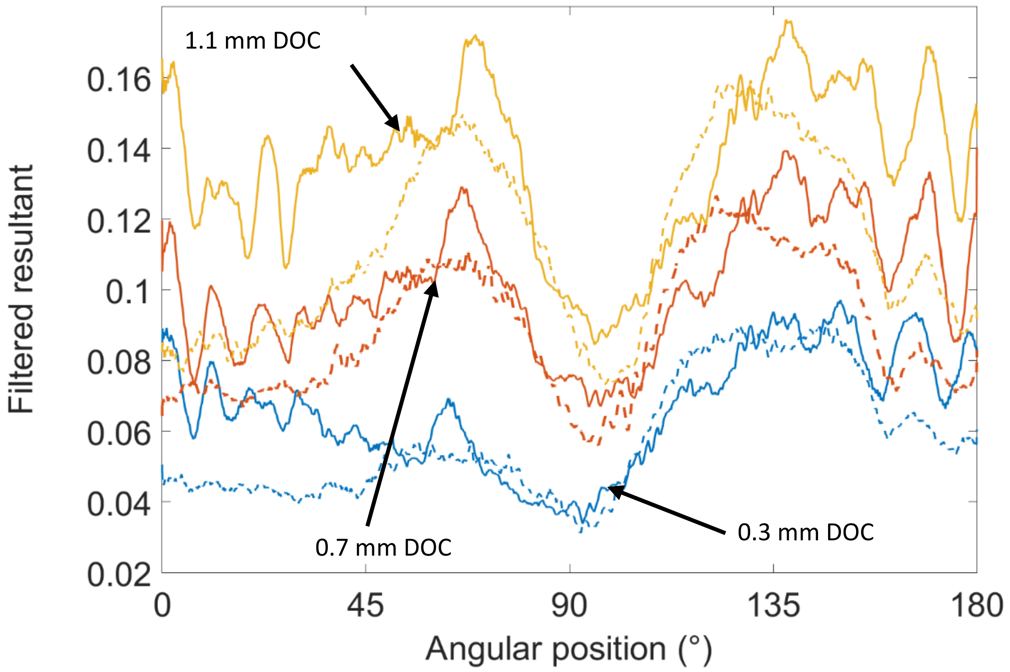


Figure 3: Filtered cutting forces normalized by the engaged blade length when machining unmodified (continuous line) and thermally modified (dashed line) wood. In the lower part with a depth of cut (DOC) of 0.3 mm, in the upper part of 1.1 mm and in the middle of 0.7 mm.

It can observe, as expected, a clear trend of increased cutting forces with increasing both for unmodified and thermally modified wood. A clear difference in cutting forces related to wood anisotropy can also be observed when machining at different angular positions. The minimum force is reached when machining along the grain (angular position 90°) while the maximum is got when machining against the grain (angular position between 14 and 160°). These results are coherent with previous investigations conducted on maple (Costes *et al.* 2004) and Douglas fir (Goli *et al.* 2010). Repeatable trends between unmodified and thermally modified wood can also be observed for the different *DOC*s. In particular, it can be concluded that the forces acting when machining, either modified or unmodified wood, along the grain are very similar (*i.e* around Φ=90 °C). On the other hand, while machining with or against the grain, thermally modified wood shows much lower cutting forces compared to unmodified wood.

CONCLUSIONS

The proposed experimental set up has shown to work fine even if at present the data analysis should be improved. The use of filtering at the beginning of the data treatment allows to compare cutting forces while machining modified and unmodified wood and to investigate the impact of grain orientation. The method is proved to be relevant to study the impact of thermal modification of wood on cutting forces. However, the analysis procedure presented in this work does not allow to conclude quantitatively on the real cutting forces applied on the tool since a strong filtering tends to reduce the measured signal’s amplitude. To do so, more suitable data analysis technics are currently under development.

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Properties of MMA treated thermally modified Norway spruce wood

Boštjan Lesar[1,4], Luka Škrlep[2], Miha Humar[3]

[1]University of Ljubljana, Biotechnical Faculty, Dept. of Wood Science and Technology Jamnikarjeva 101, SI-1000 Ljubljana, Slovenia [email: bostjan.lesar@bf.uni-lj.si]
[2]Slovenian Slovenian National Building and Civil Engineering Institute, Dimičeva ulica 12, 1000 Ljubljana [email: luka.skrlep@zag.si]
[3]University of Ljubljana, Biotechnical Faculty, Dept. of Wood Science and Technology Jamnikarjeva 101, SI-1000 Ljubljana, Slovenia [email: miha.humar@bf.uni-lj.si]
[4]Slovenian forestry institute, Večna pot 2, SI-1000 Ljubljana, Slovenia

Keywords: contact angle, decay, mechanical properties, methyl methacrylate, Norway spruce, Thermal modification

ABSTRACT

Heat-treatment is one of the most important and commercially successful modification process. The aim of the present research was to improve mechanical properties of thermal modified (TM) Norway spruce (*Picea abies*) wood by additional treatment of TM wood with methyl methacrylate (MMA). After conditioning, contact angle (CA), short-term and long-term water uptake, bending and compression strength and performance against wood decay fungi (*Trametes versicolor*, *Gloeophyllum trabeum* and *Fibroporia vaillantii*) of the thermally modified MMA treated spruce wood were determined. Treatment of thermally modified wood with MMA has a positive effect on the resistance against tested wood decay fungi. Analysis of mechanical properties showed positive effect of MMA treatment on compression and bending strength. Results of the present research show that MMA treatment of TM wood that was modified at milder processes, can be useful method to enhance one of the biggest issue of thermally modified wood.

INTRODUCTION

Importance of wood as a building material is increasing in the recent decades in most of the Central Europe. Fact, that the majority of the European wood species has non-durable wood, limits usage of wood in outdoor applications. In order to use wood outdoor, proper protection measures have to be applied. In the past, biocidal products were preferred method of wood protection (Pernak *et al*. 2005). Nowadays, consumers are demanding non-biocidal solutions for prolonging of service life.

Wood modification was identified as one of the approaches for improvement of relevant properties of wood without use of biocides. Thermal modification (TM) is one of the most commercially important modification procedures (Esteves and Pereira, 2008). Based on the data of Welzbacher and Scheiding (2011), there is between 250.000 and 300.000 m^3 of thermally modified wood produced annually in Europe. Beside positive effects thermal modification also mechanical properties of wood are degraded. The effect on MOE is small, whereas static and dynamic bending strength and tensile strength decreases considerably (Esteves and Pereira, 2008, Bal 2014). This is reason that in practice, thermally treated wood is predominantly used in cladding and decking applications (Ormondroyd *et al.* 2015) and not for outdoor constructions.

Consequently, various functional monomers have been explored to improve wood durability, increase mechanical properties or give dimensional stability to non-durable soft or hardwoods (Zhang *et al*. 2005, 2006, Ding *et al*. 2013, Mattos *et al.* 2015). Methyl methacrylate MMA is one of the most inexpensive and accessible monomers in the market, mainly due to large production in Asia, and compatibility with other monomers (Ding *et al*. 2013). In all studies wood was impregnated with liquid monomers and in situ polymerized.

The aim of the present research was to improve mechanical properties of thermal modified Norway spruce (*Picea abies*) wood by additional treatment of TM wood with MMA in order to reduce the consumption of polymer and reach good penetration of monomers into the wood, MMA was introduced in impregnation chamber in gaseous phase.

EXPERIMENTAL

Materials

For our experiment Norway spruce (*Picea abies*) wood (sawn boards) was thermally modified according to Silvaprodukt commercial procedure (Silvapro®) at 210 °C and 230 °C (Rep *et al.* 2004). After modification samples for all the tests was prepared. Thermal modification samples were dried at 103 ± 2 °C until constant mass. Afterwards samples were treated with MMA according to three different procedures, with different concentrations of MMA with and without inhibitor (Phenothiazine). The variables in the procedures of impregnation were; time, temperature and pressure (Table 1). Treated samples was dried at 103 ± 2 °C and weight percentage gain (WPG) was calculated. Conditions in impregnation chamber were optimized to keep MMA in gaseous phase during impregnation process. All sizes of samples were modified at the same time. After modification, and MMA treatment the specimens were conditioned for 4 weeks in laboratory conditions.

Table 6: Variation of MMA impregnation of thermally modified Norway spruce

Samples mark	Treatment
A	vacuum 15 min, injection of MMA with 1 % inhibitor (Phenothiazine), 4 h pressure 5 bar at 150 °C, cooling to room temperature
B	vacuum 15 min, injection of MMA without inhibitor, 6 h pressure 6 bar at 160 °C, cooling to room temperature
C	vacuum 15 min, injection of MMA with 1 % inhibitor (Phenothiazine), 20 h pressure 9 bar at 120 °C, cooling to room temperature
D	TM control
E	Unmodified Norway spruce treated with MMA - control

Methods

After conditioning contact angle (CA), short-term and long-term water uptake, bending and compression strength and performance against wood decay fungi of the thermally modified MMA treated spruce wood were determined.

Contact angle measurements (CA)

The sessile drop method was applied used to determine the contact angles of distilled water on the surfaces of specimens with a Theta optical tenziometer from Biolin Scientific Oy (Espoo, Finland). After calibration, the goniometer microscope was focused and adjusted on the image of a drop. The contact angles were measured by Young-Laplace contact angle analysis mode in OneAttension software version 2.4 (r4931) (Biolin Scientific). The shapes of drops were observed in an optical goniometer and recorded by a digital camera installed in the axial extension of the lens (Humar *et al*. 2016). Droplets of 4 μL were applied at three different places 10 mm apart from each other on the radial surface of ten parallel specimens (1.5 × 2.5 × 5.0 cm^3). In total 30 contact angles were determined per material/aging procedure. The image recording was set for 62 s (15 FPS), and the time when the contact angles started to be calculated (0 s) was after detachment of the dispenser tip from the drop, which happened approximately 2 s after the first contact of the drop with the substrate. The measurements were taken at a constant temperature of 23°C.

Short-term capillary water uptake test

Measurements were carried out at room temperature of 20 °C at a relative humidity (RH) of 50 ± 5 %, on a Tensiometer K100MK2 device (Krüss, Hamburg, Germany), according to a modified EN 1609 (CEN 1997) standard, after conditioning at 20 °C and 65 % RH until constant mass. The axial surfaces of the specimens (1.5 × 2.5 × 5.0 cm^3) were positioned to be in contact with the test liquid (distilled water), and their masses were subsequently measured continuously every 2 s for 200 s. Other parameters used were: velocity before contact 6 mm/min, sensitivity of contact 0.005 g, and depth of immersion 1 mm. Depending on the final weight of the immersed sample and the square surface of the axial surface of specimens, the uptake of water was calculated in grams per square cm. Ten treated and ten untreated control spruce wood samples were used for this analysis.

Long-term liquid water uptake test

Long-term water uptake test was prepared according to floating test prescribed by EN 16818, (2015) standard. Samples of dimensions (4 × 4 × 2.5 cm^3) have been specially prepared for a floating test, with end sealed edges with two component epoxy coating. The bottom and upper (largest) surfaces of the sample were uncoated. Before floating test, specimens were oven-dried at 103 ± 2 °C until constant mass and weighed to determine the oven-dry mass. The samples were floated in a deionized water, ensuring that the upper surfaces are not wetted. Measuring interval was in accordance with the above mentioned standard 1 h, 4 h, 8 h, 24 h, 48 h, 72 h and 114 h. Ten treated and ten untreated control spruce wood samples were used for this test.

Water Vapour Uptake in a Water-Saturated Atmosphere with drying process above freshly activated silica gel

In addition to liquid water uptake, wood also absorbs water from the air. An experiment was performed to determine the performance of wood in a climate with high relative humidity. Specimens (1.5 × 2.5 × 5.0 cm^3) were oven-dried at 103 ± 2 °C to a constant mass and weighed to determine oven-dry mass. The specimens were stacked in a glass climate chamber with a ventilator above distilled water. Specimens were positioned on plastic mesh above the water using thin spacers (Meyer-Veltrup *et al*. 2017). After 24 h of exposure, they were weighed again, and their moisture content was calculated. Specimens were then left in the same chamber for an additional 3 weeks until a constant mass was achieved. Afterwards, samples were transferred to container with freshly activated silica, after 24 h samples was weighed. Ten treated and untreated 10 controls spruce wood samples were used for this analysis.

Durability test against wood-destroying basidiomycetes

The decay test was performed according to mini block procedure with samples (1 × 1.5 × 3.0 cm^3). Conditioned specimens (samples were conditioned in laboratory conditions prior exposure for 3 to 4 weeks) were steam-sterilized in an autoclave before exposure to wood decay fungi; 350 mL experimental glass jars with aluminum covers and cotton wool with 50 mL of potato dextrose agar (DIFCO) were prepared and inoculated with white rot fungi *Trametes versicolor* (L.) Lloyd (ZIM L057) and two brown rot fungi (*Gloeophyllum trabeum* (Pers.) Murrill (ZIM L018) and *Fibroporia vaillantii* (DC.) Parmasto (ZIM L037). One week after inoculation, two specimens per jar were positioned on a plastic HDPE mesh, which was used to avoid direct contact between the samples and the medium. The assembled test glasses were then incubated at 25 °C and 80% relative humidity (RH). After incubation, specimens were cleansed of adhering fungal mycelium, weighed to the nearest 0.0001 g, oven-dried at 103 ± 2 °C, and weighed again to the nearest 0.0001 g to determine mass loss through wood-destroying basidiomycetes. Five samples per treatment and five untreated controls were exposed to each fungi.

Mechanical Properties

Static three-point bending tests were performed according to the EN 310 standard (CEN 1993) on a Zwick-Roell Z100 universal testing machine (Zwick-Roell, Ulm, Germany) to obtain the modulus of elasticity (MoE - bending) and bending strength (F_m – bending strength). Ten replicates for each modification/impregnation and ten controls with dimensions 360 × 20 × 20 mm^3 were prepared and conditioned in a standard climate (relative humidity = 65 ± 5%; temperature = 20 ± 2 °C) until a constant mass of the specimens was achieved. The specimens were tested for MoE and F_m immediately after incubation in the standard climate.

Compressive strength (F_m - compression) was determined according to the ASTM D1037-12 (2012) standard on a Zwick-Roell Z100 universal testing machine (Zwick-Roell, Ulm, Germany). Ten replicates for each modification/impregnation and ten controls with dimensions 20 × 20 × 50 mm^3 were prepared and incubated in a standard climate until a constant mass of the specimens was achieved. The specimens were tested for compressive strength immediately after incubation in the standard climate. After the test, the compressive strength (F_m) was calculated.

RESULTS AND DISCUSSION

Wight percentage gain

Weight percentage gain (WPG) was calculated, to get the first information about interactions between MMA and thermally modified Norway spruce wood. In addition, we tend to correlate WPG with other relevant properties. During treatment with MMA different conditions were established in the chamber, however MMA was always introduced in chamber in gas phase. Results showed clear difference between different treatments and sample sizes. The most promising results were determined after treatment procedure C (treatment at low temperature) for the majority of the sample dimensions tested (Table 6). Compared to other treatments, a treatment procedure C the initial temperature is increased as well as the final pressure. It can be assumed, that the increased pressure and the reduced temperature in the chamber positively affected reactions and penetration of MMA into the wood. It is assumed that at the lower temperature MMA did not polymerise in the chamber, but it penetrated into the wood and polymerized there. Treatment (B) cannot be compared with others, as during the MMA treatment, some samples were charred, what resulted in smaller or even negative WPG. Due to the presence of oxygen in the chamber and high temperatures, additional oxidation and coagulation occurred. It is assumed that during the process there was some additional thermal degradation going on due to the presence of oxygen, which resulted in additional mass loss.

Table 7: Weight percentage gain of different samples

Test/ Samples dimensions (cm)	**MMA treatment**	**TM =230 °C**	**TM =210 °C**	**Unmodified control**
		WPG of MMA [%]	**WPG of MMA [%]**	**WPG of MMA [%]**
Floating 4×4×2.5	A	2.2	0.3	/
	B	1.8	1.2	/
	C	2.7	4.0	/
	D	0	0	/
Bending 2×2×36	A	2.0	2.7	/
	B	2.2	0.3	/
	C	2.4	2.3	/
	D	0	0	/
Compression 2×2×5	A	3.6	5.8	/
	B	-0.1	-0.6	/
	C	2.1	1.3	/
	D	0	0	/
Sorption tests 1.5×2.5×5	A	2.1	1.7	/
	B	1.1	-3.0	/
	C	2.4	1.8	/
	D	0	0	/
Durability 1×1.5×3	A	1.0	0.7	-2.5
	B	-0.8	-3.9	-8.8
	C	2.1	1.5	0.7
	D	0	0	0

Durability against wood-destroying basidiomycetes

During durability test all the fungi were active. Untreated control samples in average lost between 17.7 % (Fv) and 24.7 % (Gt) of the initial masses (

Table ***8***). As expected, thermal modification (D) itself contributed to better durability against wood decay fungi than control samples. In our study wood decay resulted in higher mass loss of the samples modified at 230 °C compared to the parallel ones modified at 210°C. This is in contrast to other studies (Welzbacher *et al.* 2007, Esteves and Pereira 2009, Candelier *et al.* 2016,), and we were not able to determine the reasons for this phenomena. Treatment of thermally modified wood with MMA has a positive effect on the resistance against tested wood decay fungi. The lowest mass loos (under 3 %) was determined at sample TM at 210 °C and MMA treated at highest temperature procedure (B). But this samples was somehow degraded during the MMA treatment (-3,9 % - 0,8 %). On the other hand mass loss of TM and MMA treated samples according to procedure C, exhibited rather good durability toward brown rot fungi, as the mass loss of the samples after exposure was lower than 3 %. Reasons for better resistance of these samples is not fully elucidated, but can be surly partially ascribed to sorption properties of MMA treated wood.

Table 8: Mass loss of MMA treaded thermally modified Norway spruce wood exposed to fungi according to mini block procedure

TM	MMA treatment	Mass loss [%]		
		Gt	Fv	Tv
230 °C	A	16.2	7.6	9.5
	B	3,6	18,5	3,2
	C	2,2	5,2	28,7
	D	16,4	12,4	21,2
210 °C	A	5.2	9.4	4.5
	B	1.9	2.1	2.5
	C	2.4	11.2	4.5
	D	15.9	7.0	6.5
-	A	4.4	10.2	5.5
	B	1.4	2.8	2.8
	C	11.2	14.6	7.8
	control	24.7	17.7	21.1

Sorption properties and water performance

As mentioned above one of the reasons for better fungal durability can assigned to reduced water absorption. Lower liquid water uptake was observed during short-term and long-term uptake. In addition to reduced liquid water uptake, MMA treatment resulted in higher contact angels as well. This can be evident at all MMA treated samples. Higher CA was evident at to untreated controls and TM samples. It should be considered that surface of MMA treated samples exhibited hydrophobic effect for longer time. (Data are not shown because lack of space.) MMA treatment has no influence on the absorption of water vapour and drying of samples above silica (**Fout! Ongeldige bladwijzerverwijzing.**). Good vapour permeability of MMA treated TM wood is on the other hand beneficial at outdoor, above ground applications (use class 3). This effect is likely to enable faster drying of treated wood. Similarly as reported for other relevant properties, the higher effect on the sorption properties was result of the treatment procedure B. However, it should be considered, that this procedure resulted in rather prominent mass loss during MMA treatment, what limits its commercial value. For sorption properties other two procedures (A and C) show promising results for further investigation as well.

Mechanical Properties

The main aim of present research was to evaluate influence of MMA treatment of thermally modified wood on mechanical properties. Results showed minor effect of MMA treatment on compression and bending strength. The only exception can be found at MMA treated samples that were modified at 210 °C prior MMA modification. In this case bending strength of MMA treated samples was improved for 20 % (Table 5). This results show that MMA impregnation of TM wood modified at milder processes, has a potential to improve mechanical properties of thermally modified wood. Further investigations are required to optimize respective treatment procedure. As expected mechanical analysis clearly show additional degradation of TM samples treated according to procedure B. Bending strength was reduced for 3 % to 11 % in comparison to TM treated samples only.

Table 9: Sorption properties of MMA treated and untreated thermally modified Norway spruce wood

TM	MMA treatment	Contact angle [60 s]	Short term water uptake [kg/m^2]	Liquid water uptake [%]		Water vapour uptake [%]		Drying above silica
				1 h	144 h	24 h	3 weeks	24 h
230 °C	A	115	20.1	8.8	9.5	5.7	13.1	6.0
	B	118	10.8	12	13.1	5.7	13.0	5.9
	C	115	28.9	9.8	10.7	6.0	15.3	6.7
	D	95	102.4	10.2	11.1	5.9	15.3	6.0
210 °C	A	115	74.4	7.7	8.4	6.3	15.1	6.9
	B	113	30.7	6.4	7.2	5.2	12.7	5.5
	C	116	62.9	8.7	9.7	6.5	17.2	7.5
	D	69	100.9	9.3	10	6.8	16.8	6.9
-	control	18	147.1	-	-	10.1	26.0	10.9

Table 10: Mechanical properties of MMA treaded thermally modified Norway spruce wood

TM	MMA treatment	Bending strength		Compression strength
		MOE [N/mm^2]	F$_m$ [N/mm^2]	F$_m$ [N/mm^2]
230 °C	A	10547.7	68.0	59.3
	B	9277.0	63.6	61.6
	C	12303.0	79.5	67.8
	D	11983.1	65.7	66.8
210 °C	A	9960.3	63.3	48.8
	B	10040.6	64.6	42.2
	C	10406.7	71.9	50.4
	D	10584.1	72.7	50.1

CONCLUSIONS

Treatment of TM wood with MMA in gas phase can be promising method for enhance mechanical, durability properties and sorption of TM wood. Results differ between treatment procedures. Additional research will be needed to optimize MMA treatment procedures for optimal properties of thermally modified MMA treated wood.

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Differential expression of *Postia placenta* wood decay genes in modified wood

Rebecka Ringman[1], Annica Pilgård[2], Martina Kölle[3] and Klaus Richter[4]

[1]RISE Research Institutes of Sweden, Box 857, 501 15 Borås, Sweden [email: rebecka.ringman@ri.se)]
[2]RISE Reasearch Institutes of Sweden and Technische Universität München, Winzererstraβe 45, 80797, München, Germany [email: annica.pilgard@ri.se)]
[3]Technische Universität München, Winzererstraβe 45, 80797, München, Germany
[email: koelle@hfm.tum.de]
[4]Technische Universität München, Winzererstraβe 45, 80797, München, Germany
[email: richter@hfm.tum.de]

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ABSTRACT

The aim of this study was to investigate the gene expression patterns of the brown rot fungus *Postia placenta* during prolonged exposure to untreated, acetylated (Ac) and furfurylated (FA) miniblock wood specimens in a soil plate decay test, analysing a wider range of genes than in previous studies (Ringman *et al*. 2014, Ringman *et al.* 2016). During the 300-day long exposure, the Ac (average WPG 22.6%) and FA (average WPG 69%) wood lost no more than 3% mass while the untreated wood reached 41% mass loss in 55 days. Expression of six genes putatively involved in the chelator mediated Fenton (CMF) degradation process (Martinez *et al*. 2009) were investigated. In conclusion, expression levels of alcohol oxidase and one laccase were significantly higher in the modified wood materials than in untreated wood, which is in accordance with previous results and may be explained by the absence of the degradation products that have been proposed to down-regulate the CMF degradation process (Zhang and Schilling, 2017). However, a copper radical oxidase and a putative quinate transporter were expressed at significantly lower levels in the modified wood materials than in the untreated wood. Previous studies have indicated a general up-regulation of genes involved in the CMF degradation process in modified wood materials compared to in untreated wood (Ringman *et al.,* 2014; Alfredsen *et al.* 2016; Alfredsen *et al.* 2016; Ringman *et al.* 2016), while the present study, including a wider range of genes, presents a more complex picture. Hence, a systemic approach is needed for future studies on the regulation of genes invovled in the CMF degradation process in modified wood.

INTRODUCTION

Brown rot fungi have been argued to be the most common and most destructive organisms involved in the degradation of softwood products (Eaton and Hale 1993). It has been hypothesised that the brown rot *Postia placenta*, as well as several other species of the orders Gloeophyllales, Polyporales and Boletales, initiate wood degradation through an oxidative process sometimes named chelator mediated Fenton (CMF) degradation (Arantes *et al.* 2012). It includes secretion and/or extracellular formation of iron reductants, oxalic acid and hydrogen peroxide, which initiate the Fenton reaction inside the wood cell wall and thereby form hydroxyl radicals that will depolymerise the polysaccharides and make them accessible for the (hemi)cellulases to degrade (Goodell *et al.* 1997; Arantes *et al.* 2012).

A significant advancement in the understanding of the regulation and spatial distribution of the brown rot CMF and enzymatic degradation processes have recently been achieved through three comprehensive studies of the spatial differences in gene expression, gene regulation and enzyme activity in the hyphal front and older parts of the mycelium in *P. placenta* and *Gloeophyllum trabeum* (Presley *et al.* 2016; Zhang *et al.* 2016; Zhang and Schilling 2017). Taken together, these studies indicate that genes proposed to be involved in CMF degradation are primarily expressed in the hyphal front. The switch to enzymatic degradation was suggested to be mediated by the degradation product cellobiose (Zhang and Schilling 2017).

Previous studies on *P. placenta* gene expression in modified wood materials have shown that genes involved in oxidative degradation of holocellulose in general are up-regulated compared to in untreated wood, while genes involved in enzymatic degradation are not (Ringman *et al.* 2014; Alfredsen *et al.* 2016; Alfredsen *et al.* 2016; Ringman *et al.* 2016). In these studies, genes encoding alcohol oxidase (Ppl118723), quinone reductase (Ppl124517), and laccase (Ppl111314) were highly expressed in *P. placenta* growing on Ac, FA, DMDHEU-treated and thermally modified wood while little or no mass loss was recorded.

The aim of this study was to examine the expression patterns of a wider range of CMF related genes in *P. placenta* compared to previous studies, during a 300-day exposure to Ac and FA wood.

EXPERIMENTAL

Wood material and fungal strain

Miniblock samples (10 x 5 x 30 (ax.) mm^3) (Bravery, 1979) of Southern yellow pine (*Pinus elliotti*, *Pinus palustri*, *Pinus echinata*, *Pinus taeda*, *Pinus rigida* and *Pinus serotine*) sapwood were acetylated or furfurylated as previously described (Larsson-Brelid, 1998; Lande *et al.*, 2008). The samples were selected based on weight percent gain (WPG) and EMC (20ºC, 65 % relative humidity (RH)), resulting in i) for Ac samples, an average WPG of 22.6 % (ranging from 19.0 % to 25.9 %) and an average EMC of 3.54 % (ranging from 2.80 % to 7.23 %), and ii) for FA samples, an average WPG of 69 % (ranging from 45.2 % to 98.3 %) and an average EMC of 4.53 % (ranging from 3.38 % to 5.56 %). The samples were leached according to EN 84 (1996) and conditioned in 20ºC/65 % RH for two weeks, after which the samples were sterilised with gamma radiation. The same set of specimens were also used in Ringman et al. (Ringman *et al.* 2017).

Decay test

Specimens were placed two by two (samples subjected to the same treatment) on sterile nets on top of sterile soil plates and subsequently inoculated with *P. placenta* (strain FPRL 280) liquid culture. Samples were incubated at 22 °C and 70 % RH. Samples exposed to fungi were harvested regularly for a period of up to approximately 300 days. Untreated samples were harvested more frequently than modified samples due to their higher mass loss rate. At harvest, the mycelia covering the wood samples were manually removed, and the samples were either i) weighed for moisture content, dried and weighed for mass loss ($n_{biol.}$=8) before being subjected sugar content analysis ($n_{biol.}$=2) (published in (Ringman *et al.* 2017)), or ii) dipped in liquid nitrogen and then stored at -80°C, awaiting molecular analysis (n=4).

RNA extraction and qPCR analysis

Wood powder from frozen samples was produced using a Mixer Mill MM 400 (Retsch GmbH, Haan, Germany) using 1.5 cm steel balls and 30 Hertz for 2 minutes. Total RNA was isolated from the wood samples and DNA was removed using the MasterPure™ RNA Purification Kit (Epicenter). RNA from each sample was converted into cDNA using TaqMan Reverse Transcription Reagents (using Oligo d(T)16) (Applied Biosystems) with 10 times the standard dNTP concentration.

Real-time quantitative PCR (qPCR) was performed on cDNA samples ($n_{techn.}$=3) using the Rotor-gene SYBRGreen PCR kit (Qiagen). Primer sequences for target genes and endogenous controls were prepared based on the genomic sequence of *P. placenta* MAD 698-R ((Martinez *et al.*, 2009) and available at http://genome.jgi-psf.org/Pospl1/Pospl1.home.html) and are listed in Table 1. Standard curves were produced, and the original concentration of each gene was calculated. All target genes were normalised to the endogenous control, β-tubulin. Significant differences ($p < 0.05$) were calculated using independent two-sample t-tests assuming unequal variances.

Table 1. Primer sequences for qPCR.

Gene annotation	Gene ID	Forward primer	Reverse primer
Alcohol oxidase (AlOx)	Ppl118723	CATCAAGAGC GCCAATCCAT	GGCGCAAAGTC AGCCTTGT
Copper radical oxidase (CRO1)	Ppl56703	CCTACCAGCT GCTTCCTGAC	AACGTTCGGCTG TATGAACC
Glucose oxidase (GOx)	Ppl108489	TCCTCGAAGCT GGAGACACCG	CGGTCTCGTAAG CCCAGTCGTAG
Quinone reductase (QRD)	Ppl124517	CGACGACAAG CCCAACAAG	GATGACGATGG CGATTTTAGG
Putative quinate transporter (PQT)	Ppl44553	GAAGGGCCGC AGTCTTGAG	GCGCTTCTCGGC CTTGA
Laccase (Lac)	Ppl111314	CATCAATGGC ACTGCAGAGC	AGCCATTCCCAG GATTCAGA

RESULTS AND DISCUSSION

Progress of wood decomposition

The specimens analysed in the present study were harvested in the decay test described in Ringman *et al.* (2017). In short, this study showed that Ac and FA samples reached a maximum of 4% and 7% ML, respectively (single samples) during the 300 days of the test period. The ML increased for 55 days in acetylated wood and 98 days in furfurylated wood. After these time points, the decay rate flattened out and the average ML for Ac was 1.44% and for FA 1.95% during the remaining part of the decay test. The untreated wood in the same experiment had 2 % mass loss after 14 days, 19 % mass loss after 28 days and reached 41% mass loss after 55 days.

Fungal gene expression

The expression of the alcohol oxidase (AlOx) gene was significantly higher in the modified wood materials compared to in untreated wood but no significant change in expression over time could be seen in either material (Figure 1). The high levels of AlOx gene expression and the lack of downregulation in the modified wood materials are in accordance with previous results and may be due to an absence of degradation products which have been suggested to down-regulate AlOx expression (Ringman *et al.,* 2014; Alfredsen *et al.* 2016; Alfredsen *et al.* 2016; Ringman *et al.* 2016; Zhang and Schilling 2017).

In the present study, the expression of two other genes proposed to be involved in H_2O_2 formation were examined (Figure 1); a copper radical oxidase (CRO1) and a glucose oxidase (GOx) (Martinez *et al*. 2009). The gene expression of CRO1 was significantly lower in the modified wood materials compared to untreated wood while there were no significant differences in GOx gene expression between the materials. No significant change in gene expression over time was seen for either of these genes in either material. Hence, the gene expression patterns of CRO1 and GOx deviated from that of AlOx. In Zhang and Schilling (2017), CRO1 was expressed at high levels at the hyphal tip after which the expression levels decreased with the age of the mycelium. The expression was also shown to be inhibited by small sugars in a similar manner to AlOx. The reason for the difference in expression levels between AlOx and CRO1 is therefore unclear.

The expression patterns of two genes potentially involved in iron reduction were examined (Figure 2); quinone reductase (QRD) and a putative quinate transporter (PQT). The QRD gene expression levels were similar in all three materials except for a peak in the untreated wood after one day of exposure (ML=0.2%). In previous studies, QRD expression results have been inconsistent in modified wood materials, which may be due to that its proposed wood mediated induction may be interfered by the wood modification (Ringman *et al.* 2014; Ringman *et al*. 2016; Zhang and Schilling 2017). No significant differences could be found between materials or over time for the expression of PQT.

The expression of one laccase (Ppl111314, Lac) was also investigated (Figure 2). This gene had significantly higher gene expression in the modified wood materials compared to in the untreated wood. No significant differences over time could be detected in the untreated wood and Ac, but a statistically significant 25-fold induction in FA was seen at 98 days (1% mass loss). These results are in accordance with previous results, apart from the induction in FA which was not seen in Schmöllerl *et al.* (2011) (Ringman *et al.* 2014; Ringman *et al.* 2016). According to Zhang and Schilling (2017), Lac is downregulated by cellobiose and other small sugars. The higher expression levels of this gene in the modified wood materials may therefore be due to a lack of degradation products.

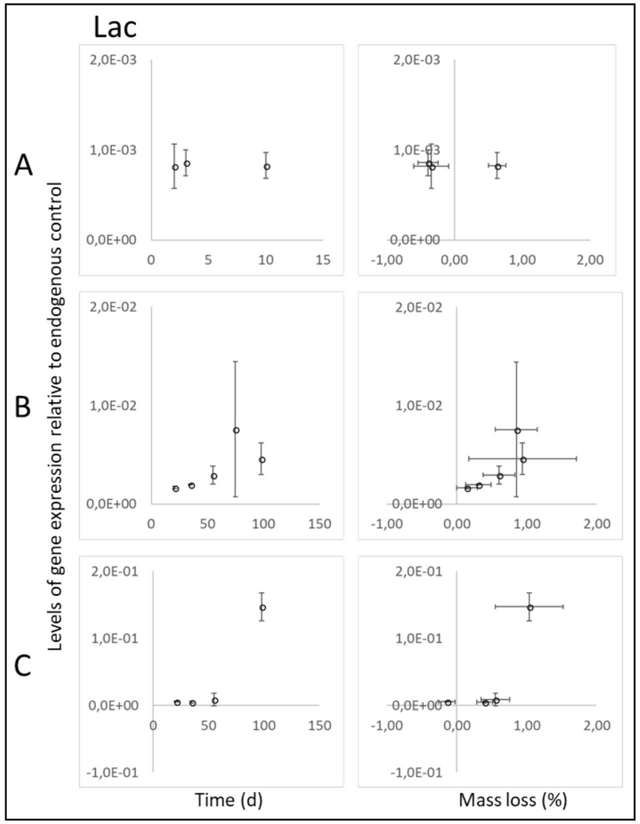
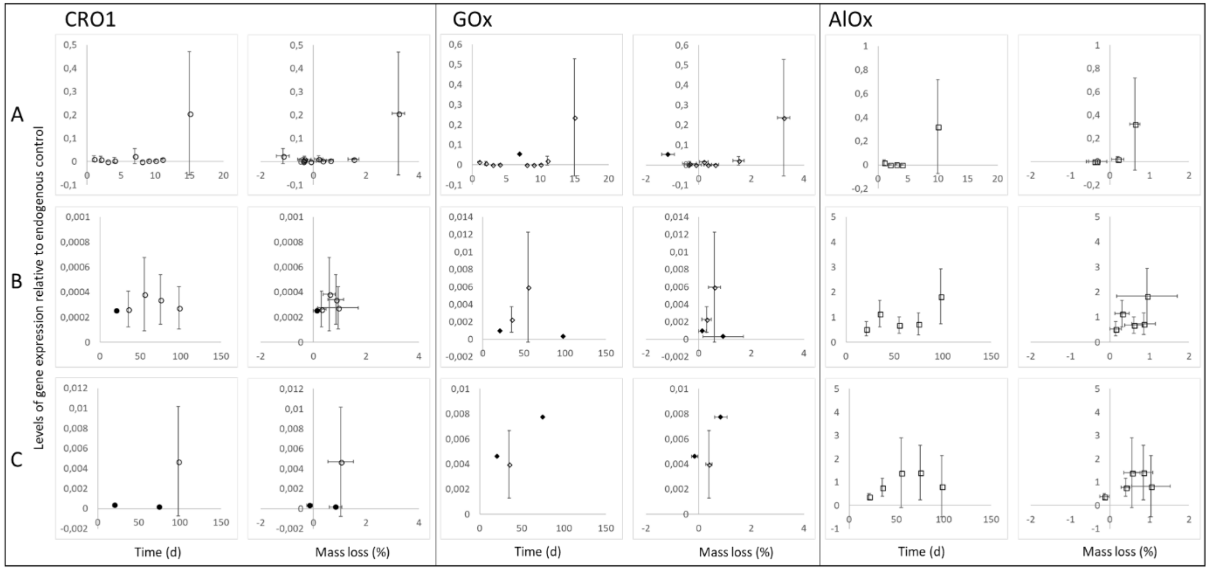


Figure 3. **P. placenta** *gene expression of Lac, relative to endogenous control, in untreated (A), acetylated (B) and furfurylated (C) wood.*



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olved in H_2O_2 formation, relative to endogenous control, in untreated (A), acetylated (B) and furfurylated (C) wood.

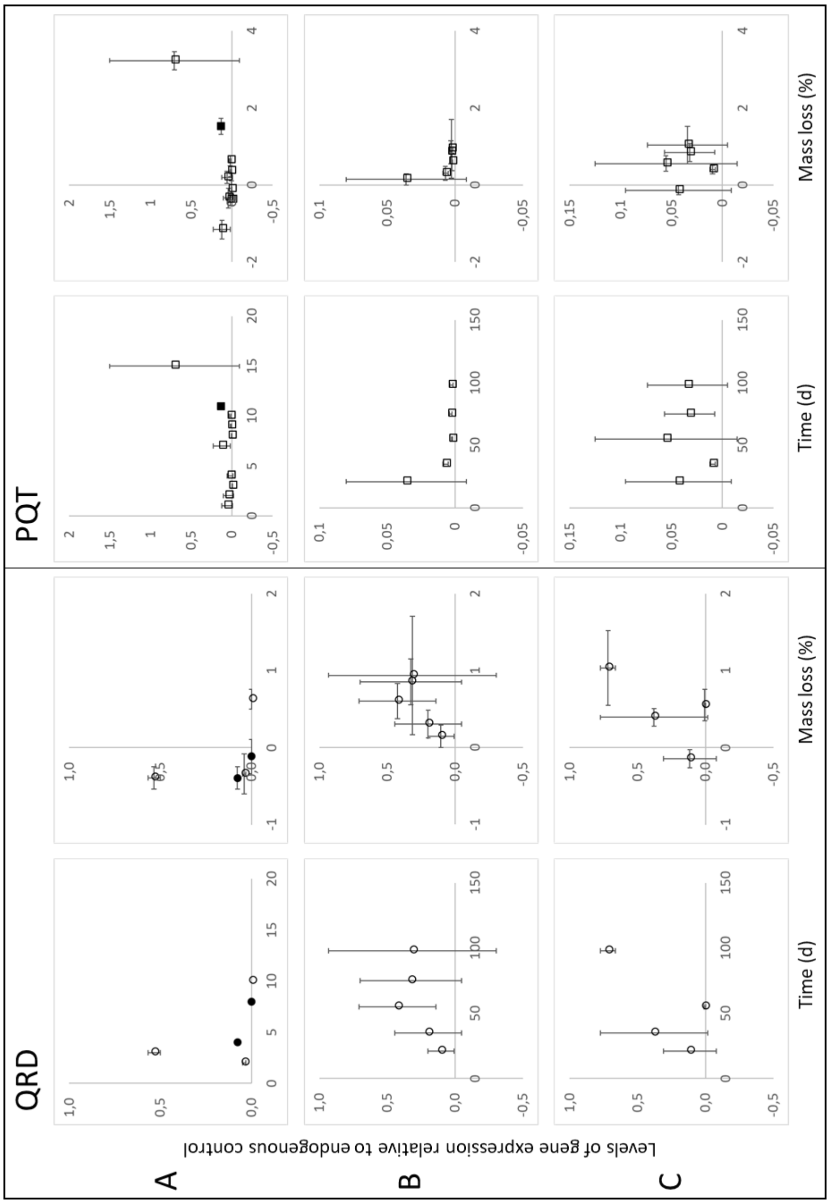

Figure 2. P. placenta expression of genes putatively involved in iron reduction, relative to endogenous control, in untreated (A), acetylated (B) and furfurylated (C) wood.

In general, previous studies have shown that the investigated genes involved in CMF degradation have been upregulated in the modified wood materials compared to untreated wood (Ringman *et al.*, 2014; Alfredsen *et al.* 2016; Alfredsen *et al.*, 2016; Ringman *et al.* 2016). This study, taking a wider range of genes involved in the CMF degradation process into account, indicates that gene regulation in modified wood materials may be more complex than an overall upregulation of CMF related genes; there is not even a consensus among genes involved in the same sub-process of the CMF degradation, as can be seen for the genes involved in the H_2O_2 formation.

The results of this study indicate that conclusions on systemic gene regulation drawn from a small set of genes may be misleading. In future studies, a holistic approach taking the whole transcriptome into account would be ideal. However, current technology makes such an approach highly time-consuming and costly when analysing multiple samples in time series, as was done in the present study. A deeper knowledge of the genes involved in the CMF degradation process and their synergies would facilitate the appropriate design of gene expression studies of selected genes in wood degradation and thereby lead to a greater understanding of their regulation in untreated and modified wood materials.

CONCLUSIONS

In conclusion, expression levels of AlOx and Lac were significantly higher in the modified wood materials than in untreated wood, which is in accordance with previous results and may be explained by the absence of the degradation products that have been proposed to down-regulate the CMF degradation process (Zhang and Schilling, 2017). However, CRO1 and PQT were expressed at significantly lower levels in the modified wood materials than in the untreated wood and the expression levels of QRD and GOx were similar in all three materials. Previous studies have indicated a general up-regulation of genes involved in the CMF degradation process in modified wood materials compared to in untreated wood (Ringman *et al.* 2014; Alfredsen *et al.* 2016; Alfredsen *et al.* 2016; Ringman *et al.* 2016), while the present study, including a wider range of genes, presents a more complex picture. Hence, a systemic approach is needed for future studies on the regulation of genes invovled in the CMF degradation process in modified wood.

ACKNOWLEDGEMENTS

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SESSION SIX B

Chemical Modification

Suitability of Lignin-Derived Monophenols to Replace Phenol in Phenol-Formaldehyde Resin for the Use in Wood Treatment

Vladimirs Biziks[1], Marco Fleckenstein[2], Carsten Mai[3] and
Holger Militz[4]

[1]Georg-August University Goettingen, Institute of Wood Biology and Wood Products, Büsgenweg 4, 37077, Göttingen, Germany [email: vbiziks@gwdg.de)]

[2]Kurt Obermeier GmbH&Co. KG, Büerghäuser Str. 70, 57319, Bad Berleburg, Germany [email: marco.fleckenstein@obermeier.de)]

[3]Georg-August University Goettingen, Institute of Wood Biology and Wood Products, Büsgenweg 4, 37077, Göttingen, Germany [email: cmai@gwdg.del)]

[4]Georg-August University Goettingen, Institute of Wood Biology and Wood Products, Büsgenweg 4, 37077, Göttingen, Germany [email: hmilitz@gwdg.de)]

Keywords: mono-aromatics, replacement of phenol, resol type resin, wood treatment

ABSTRACT

A pyrolysis oil or bio oil can be obtained by thermal decomposition of technical lignin in addition to solid residues. Due to the heterogeneity of the lignin macromolecule, the oil contains a large variety of organic compounds, mainly mono-aromatics, which are proposed to be used for replacement of phenol in phenol-formaldehyde (PF) resins. Therefore, the goal of this study was to assess the suitability of mono-aromatic cleavage products of lignin for substitution of petroleum based phenol in PF resin synthesis and usage of new resin for wood treatment. For this purposes, nine of the most abundant mono-aromatic compounds of bio oils were selected: ortho-, meta-, para-cresol, guaiacol, catechol, 4-methylcatechol, resorcinol, syringol, 4-ethylphenol to synthesise resol type resins from each mono-aromatic. Relevant features of the resins such as pH, viscosity, average molecular weight and curing behaviour using differential scanning calorimetry (DSC) were analysed. Weight percent gain (WPG), bulking and dimensional stability were determined and compared with the phenol-formaldehyde treated wood. Scots pine (*Pinus sylvestris*) sapwood samples were used to evaluate the suitability of resin for wood treatment in terms of dimensional stability. Resins made of guaiacol, ortho-, meta-, or para-cresol and of 4-methylguaiacol proved to be suitable for wood treatment, whereas resin made of catechol, 4-methylguaiacol and of syringol did not. The suitability of mono-aromatics for synthesis of resol type resin depends on the chemical structure, where the reactivity of the mono aromatic (derivative of hydroxybenzene) is defined by the type, location and amount of substituents.

Mono-functional phenols like syringol and 4-methylguaiacol have only one free position available for hydroxymethyolation and result in di-phenyl compounds, which are not able to develop 3D polymers (do not polycondensate). In contrast, suitable resins can be synthesized from di-, tri and tetra-functional phenols such as cresol, guaiacol and 4-ethylphenol and used for wood treatment.

INTRODUCTION

In the pulp and paper industry about 80 million tons of lignin are produced annually as by product (Pradhan *et al*. 2015), which is generally used to regenerate the chemicals during black liquor burning, however some side streams are used to isolate the lignin out of black liquor (Wang *et al*. 2013). Until now, lignin has been applied in different studies in the field of wood-based panel manufacture, for example, it was used both as a filler and crude oil-based phenol substitute in phenol formaldehyde (PF) resins. 30% PF resin can be substituted by lignosulfonates in plywood manufacturing. The physical-technological properties of the manufactured plywood with lignin phenol formaldehyde (LPF) adhesives were comparable with the boards using control PF adhesive (Roffael *et al*. 1974). Later (Klašnja and Kopitović 1992) substituted 50% PF resin with Kraft lignin and obtained plywood with satisfactory shear strength. But the limitations of lignin in PF resin substitution such as high molecular mass up to 50.000 g mol-1, (Puls 2009) only a moderate reactivity, (Pizzi 1994) negative steric effects because of the macromolecular complex structure and functional groups on the aromatic ring, mainly methoxy or other ethers, (Chen *et al*. 2013, Vishtal and Kraslawski 2011) required long press time and high press temperatures. For these reasons, the application of lignin as PF substitute or filler in adhesives is commercially not attractive and only a few industrial applications have been implemented (Hemmilä *et al*. 2013, Chen *et al*. 2013).

A novel scientific approach is the application of lignin in the field of chemical wood modification. For this application, the reactive chemicals have to penetrate through the micropores into the wood cell wall, build up a stable network to improve dimensional stability, biological durability and weathering resistance of the modified wood (Hill 2006). There are specific requirements for the modification chemicals. They have to be reactive enough to build up a stable network and have to be small enough to penetrate through the micropores in the wood cell wall. The maximum diameter of the cell wall micropores in water-swollen state are in the region of 0.5 nm – 4.0 nm (Donaldson *et al*. 1988, Stone *et al*. 1965). For these reasons macromolecule of technical lignin cannot be applied in the field of wood treatment and have to be initially depolymerized into low molecular weight phenols.

Different catalysts (base, acid or metallic catalysts), ionic liquids and supercritical fluids were used to depolymerize the complex lignin structure (Wang *et al*. 2013). Furthermore, pyrolytic cleavages either by conventional or microwave heating were also used (de Wild *et al*. 2014, Mudraboyina *et al*. 2015). The products obtained are gases, solid residue and liquids, which contain the low molecular weight phenols. The catalytic lignin depolymerization is the most important cleavage reaction. (Bengoechea *et al*. 2015) used different types of catalysts to cleave the lignin macromolecular structure of kraft lignin. They were able to cleave lignin into low molecular weight compounds with molecular weight (M_w) in the range of 211 to 397 g mol-1. Differences in M_w depend on the catalyst used. Previously, (Forchheim *et al*. 2012) evaluated the influence of Raney Nickel catalyst on the formation of intermediates in lignin depolymerization. In total 13 hydrothermal depolymerization experiments of enzymatic hydrolysis lignin were performed with and without Nickel catalyst at different reaction times and reaction temperatures. Depending on the process parameters, different amounts of bio-oils were obtained. Highest yield of detected mono-aromatic lignin degradation products were 24.9 mg g-1 lignin when using Nickel catalyst at 673K for 0.5h. The detected mono-aromatic phenols are phenol, catechol, guaiacol, o-cresol, p-cresol, 4-methylcatechol and 4-methylguaiacol. Due to the heterogeneity of the lignin macromolecule, the oil contains a large variety of organic compounds, mainly mono-aromatics, which are proposed to be used for replacement of phenol in phenol-formaldehyde (PF) resins. Therefore, the goal of this study was to assess the suitability of mono-aromatic cleavage products of lignin for substitution of petroleum based phenol in PF resin synthesis and usage of new resin for wood treatment.

EXPERIMENTAL

Chemicals

The following chemicals from Sigma-Aldrich Chemie (Munich, Germany) were used in this study: phenol (≥99%), ortho-cresol (≥ 99%), meta-cresol (≥ 98%), para-cresol (≥ 99%), 4-ethylpenol (≥ 98%), catechol (≥ 99%), guaiacol (≥ 99%), syringol (≥ 98%), resorcinol (≥ 99%), 4-methylcatechol (≥ 95%), a aqueous formaldehyde solution (37%), ethanol und a aqueous sodium-hydroxide solution (50%). Phenol (≥ 99%) serves both as a reference substance and as a cleavage product from lignin.

Synthesis of the Resols

Every aromatic compound was hydroxymethylated under alkaline reaction conditions, whereby the molar ratio of formaldehyde to phenol was kept constant for each synthesis at 1.5 and that of sodium hydroxide to phenol at 0.1. During each synthesis the measured amount of aromatic compound and aqueous sodium hydroxide solution was weighed out in a 500ml 4-neck flask equipped with a thermometer, dropping funnel, reflux condenser and stirrer. For better homogenization 5g of ethanol were weighed into the flasks. The 4-neck flask was rinsed with nitrogen and subsequently submerged in a 75°C oil-bath. As soon as the temperature in the flask reached 65±2°C, the aqueous formaldehyde solution was added slowly via a drip over a 30 minute period. The reaction temperature was kept constant at 65±2°C during the entire reaction period (4h), whereby nitrogen was constantly being added. The resol synthesis was ended by submerging the flask in an ice bath and allowing the resol to cool down quickly to room temperature.

Characterization of the Resols

The non-volatile part (NVC) of the synthesized resols was determined by mixing approximately 2g of resin with 2g of n-butanol in an aluminum dish and then keeping it at 140°C until it completely hardened within a 4h period. The NVC in the resols was determined for the resol mass before hardening and for the hardened mass thereafter. A pH-meter (Mettler Toledo, Gießen, Germany) with a glass-reference electrode was used to measure the pH-value of the synthesized resols (45% NVC) at 22±2°C. The viscosity of the synthesized resols (45%NVC; 22±2°C) was ascertained through use of a Visco Tester 7L (Haake Technik GmbH, Vreden, Germany). The hardening properties of the synthesized resols were evaluated by using a dynamic difference calorimeter DSC 200 F3 (Netzsch-Gruppe, Selb, Germany). For each of the samples 20mg of the synthesized resols (45% NVC) were weighed into a respective gold-crucible. Each was then heated from 0°C to 250° at a heating rate of 20°C min^{-1}. Using the Proteus evaluation program we determined the initial, peak and final temperatures as well as the integral of the thermo-grams.

Wood Treatment

For each group 10 samples of pine (Pinus sylvestris L.) sapwood with dimensions of 10 x 10 x10 mm^3 (radial x tangential x longitudinal) were used for treatment with resin. The samples were dried at 103±2°C until constant weight and then cooled to room temperature in a desiccator. The dry weight and dimensions (radial x tangential) of the samples were measured. The samples were impregnated in a vacuum (10 kPa, 30 min) with the impregnation solutions (20% NVC: with water as a solvent) and subsequently left in the solution for an additional 4h at normal atmospheric pressure. Following the impregnation the samples were slowly dried (at 25, 45, 60, 80, and 103°C; each step = 8h) before completely hardening the resins in a final step at 140° for 1h. The weight gain of the samples, i.e., the weight-percent-gain (WPG) was calculated according to (Militz 1993). The maximum swelling of the samples after impregnation was calculated according to (Mantanis *et al*. 1994), whereby the area (radial x tangential) of the samples was used instead of the volume. The relative cross-sectional bulking-coefficient (rBC) was calculated as (Eqn.1):

$$rBC = BC_A / aBC_{PF} \qquad (1)$$

whereby BC_A represents the cross-sectional bulking of the modified samples (Klüppel and Mai 2013) and aBCPF stands for the median of the increase in area (radial x tangential) of the modified samples with PF-resin. The relative dimensional stability (rASE) was determined according to the following equation (Eqn. 2):

$$rASE = ASE_A / aASE_{PF} \qquad (2)$$

whereby ASE_A is the dimensional stability of the modified samples according to Hill (2006) and $aASE_{PF}$ represents the median of the dimensional stability of the modified samples with PF-resin.

RESULTS AND DISCUSSIONS

The use of resols in the wood treatment is based on the assumption that the monomers and oligomeric constituents in the resols are able to penetrate the cell wall and develop a stable network (Rowell 2005). Only after the monomers and oligomeric constituents have become firmly anchored in the cell wall through chemical reactions (condensation reactions) does an increase in the modified wood occur with regard to its dimensional stability, biological longevity and resistance to weather (Hill 2006).

The rBC reveals how the resols react in comparison to the PF-resol with respect to the modification of the wood cell walls.

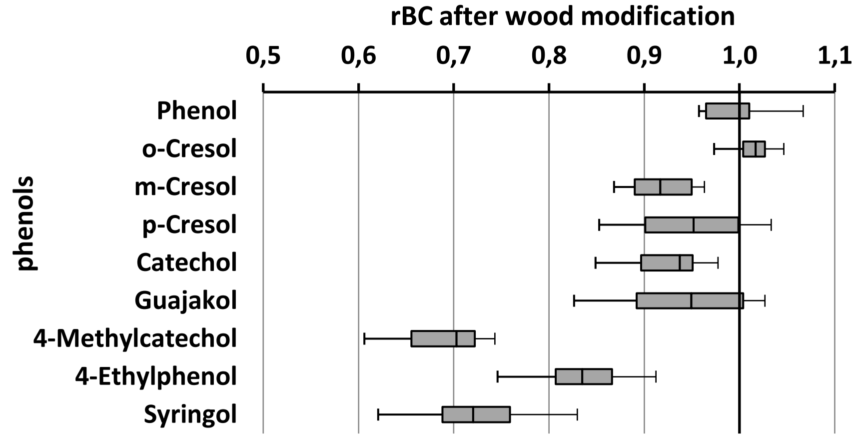

Figure 1. Relative Cross-Sectional Bulking-Coefficient (rBC) of the Resols Relative to the PF-Reference-Resin.

Although all synthesized resols are able to penetrate the wood cell wall, they do so to varying degrees (Figure 1). The absorption of monomers and oligomeric constituents into the wood cell wall is, for the most part, dependent on the hydrodynamic volume of the molecules (Rowell 2005) and the resulting solubility of the molecules in alkaline solutions (Christiansen and Gollob 1985) as well as the polarity of the monomers and oligomeric constituents in the resols (Mantanis *et al*. 1994). The maximum diameter of the micro-pores in the cell wall, through which the modification chemicals must pass to reach the actual wall, lies, in a swollen state (with water as the solvent), between 0.5 and 4.0 nm (Hill 2006; Donaldson *et al*. 1988; Stone and Scallan 1965). Only molecules with a molecular weight of approx. ≤450 g mol-1 are, therefore, able to pass through the pores and into the wood cell wall. Differences in the rBC cannot be explained by the volumes of the monomers and oligomeric constituents in the resols because the similar viscosities of the resols point to the distinct possibility that there are almost equal hydrodynamic volumes of monomers and oligomeric constituents in the resols with the exception of catechols (Table 1).

Table 1. Relevant resin properties caused by mono-aromatic phenols

Phenols	pH value	Viscosity [Pa*s]	NVC[a] [%]
phenol	10.4	0.0054	52.2
o-cresol	10.8	0.0058	53.4
m-cresol	10.4	0.0061	52.9
p-cresol	10.7	0.0052	54.1
catechol	10.4	0.0092	52.4
guaiacol	10.9	0.0054	53.1
4-methylcatechol	10.2	0.0142	53.0
4-ethylphenol	10.3	0.0057	52.1
syringol	10.7	0.0067	48.3

NVC[a] – non-volatile component

In spite of the higher viscosity (Tabable 1) there are apparently sufficient small molecules present in the catechol-resol so that the rBC amount is only approx. 5% less than in the phenol-resol. 4-methylcatechol-resol demonstrates an rBC-value which is approx. 30% below that of phenol-resol; this can be explained by the large hydrodynamic volumes of the oligomers in the resols. The penetration of the cell wall is prevented by the high molecular weight so that the oligomers remain in the lumen or on the surface of the samples. Another important factor ensuring successful wood treatment is the polarity of the monomers and oligomeric constituents in the impregnating solutions. There is a direct correlation between the swelling of the wood cell wall and the polarity of the solvent, i.e., the molecules in the impregnating solutions (Mantanis *et al*. 1994). The hydroxyl-groups are mainly responsible for the hydrophilic properties of wood (Skaar 1988) and only allow those molecules with a certain hydrophilic property to implement swelling. Penetration of the molecules into the wood cell wall is a prerequisite to creating a swollen condition within the wall. Samples which are modified with phenol-, o-, m-, and p-cresol-, catechol- and guaiacol-resols demonstrate no significant differences in their maximum swelling nor in their rBC-values. It appears that strongly hydrophilic phenol swells wood just as much as the less hydrophilic aromatics, which have, in addition to a hydroxyl-group, other substituents (methyl-, methoxy-groups). Significant differences in maximum swelling and rBC do, however, occur whenever an ethyl-substituent (4-ethylphenol) is in the para-position on the aromatic ring instead of a methyl-substituent (p-cresol). This extension results in a reduction in swelling of approx. 1.4% due to hydrophobicity. 4-methylcatechol is a relatively polar molecule and should actually produce a larger rBC-value and increased swelling. As already described, the rBC-value and the maximum swelling can be explained by the greater hydro-dynamic volumes. Syringol displays in comparison to phenol a reduction in maximum swelling of approx. 2.5% and an approx. 26% decrease in the rBC. The reason for this can be found in a reduced polarity resulting from the two methoxy-groups on the aromatic ring. A successive hydroxymethylation of the aromatic rings has a positive influence on the polarity of a molecule, whereby the position of the hydroxymethyl-group also influences polarity (Li *et al*. 2001). Hydroxymethylated molecules are more hydrophilic and therefore better suited for chemical wood modification. Finally, it should be pointed out that keeping the samples in the impregnation solutions for more extended periods of time or raising the temperature of the solution can lead to a closer alignment of the swelling values (Mantanis *et al*. 1994). To maintain a comparability of the resols in the field of chemical wood modification, the impregnation processes must remain uniform.

In all of the modified samples a decrease in the resin polymers occurs as a result of the rinsing cycles. The total loss of mass is equal to the sum of the decreases in the cell wall material and losses caused by the rinsing away of resin polymers from the surface, from the lumens or from the cell walls, whereby losses of cell wall material have been rather neglected. Samples modified with phenol-resol display the lowest loss of mass. Those modified with catechol-, o-, m-, and p-cresol-, guaiacol- and 4-ethylphenol-resol reveal a loss of mass which is 3-12% greater than in PF-resin. Samples showing the greatest loss of mass are those modified with syringol. Mono-functional aromatic compounds are completely unsuitable for a polymerization reaction, as they can only form maximum dimers (Hultzsch 1950). This is the reason for the large losses of mass during rinsing cycles. The loss of mass through resin polymers following rinsing cycles does not in and of itself shed any light on the stability of the resin polymers in the wood cell walls. The rBC after rinsing provides information with regard to the stability of the resin polymers in the cell wall relative to the stability of the phenol-polymers in the wall.

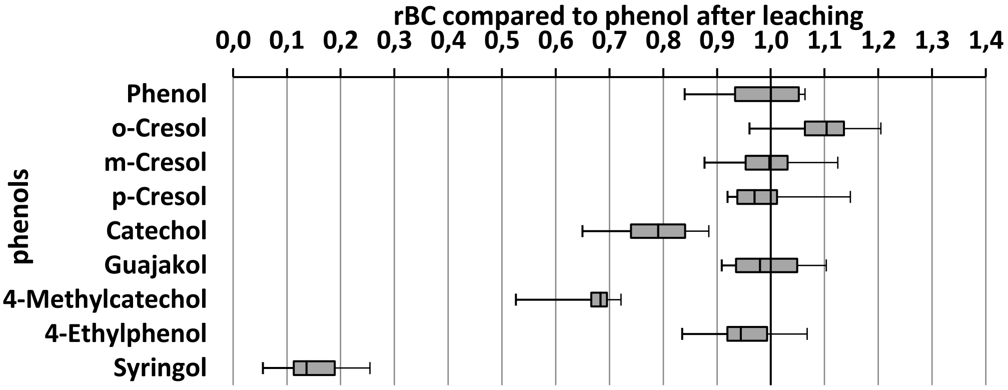

Figure 2. Relative cross-sectional bulking (rBC) resulting from the different phenols compared to standard PF resin after five saturated-dried cycles.

Evaluation of the relative stability of the resin polymers in the wood cell wall shows no significant differences among the polymers which were synthesized from phenol, cresol, guaiacol and 4-ethylphenol. Significant differences are displayed in the stability of the resin polymers in the wood cell wall by catechol-, 4-methylcatechol- and syringol-resins in comparison to polymers from PF-resin (Figure 2). The polymer stability does not directly correlate with the functionality of the aromatics. The polymers from phenol and m-cresol, which are cross-linked 3-dimensionally, do not show any significant differences in stability resulting from rinsing compared to the linearly linked polymers from p-cresol, guaiacol, and 4-ethylphenol. Molecules which link linearly are able to roll themselves into a bundle and thereby apparently increase their stability (Hultzsch 1950). The catechol- and 4-methylcatechol-polymers reveal a polymer stability which is significantly, 21% and 32%, less than that of the PF-polymer. Catechols are quickly changed in oxidation reactions into quinones through the influence of light and/or oxygen (Jacob *et al.* 2008). The quinones formed are not able to react with formaldehyde; therefore, they are also not able to form a polymer, they considerably hamper the polymerization reactions in the cell wall and promote rinsing molecules out of the wood cell wall. Polymers from syringol have in comparison to PF-polymers a stability level which is approx. 88% lower. This can be explained by the mono-functionality of syringol making it impossible for this molecule to form a polymer (Hultzsch 1950). Introducing into and fixating modification chemicals in the wood cell wall leads to an improvement in the dimensional stability because the wood is placed in a pre-swollen state through the chemical modification (bulking).

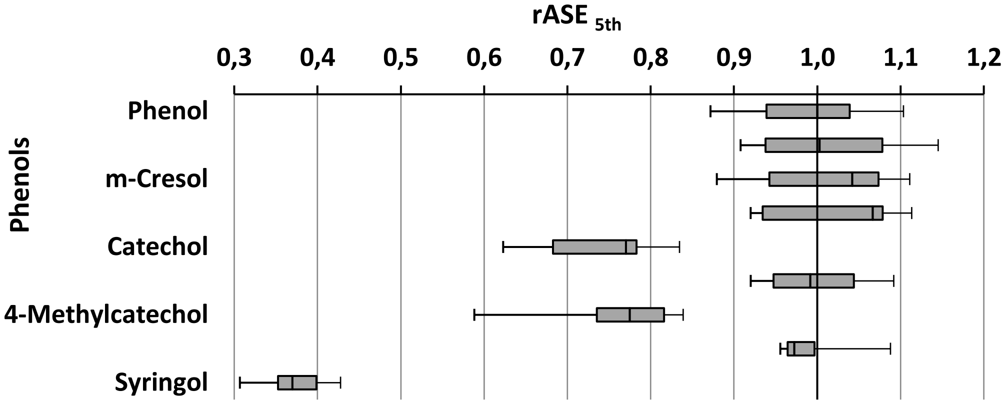

Figure 4. Relative dimensional stability of treated samples after the 5th saturated-dried cycle

Evaluation of the relative dimensional stability following the rinsing cycles (Figure 3) reveals that there no significant differences result among the samples which are treated with phenol-, o-, m-, p-cresol-, guaiacol- and 4-ethylphenol-resols. In contrast, samples treated with catechol-, 4-methylcatechol- und syringol-resols display clearly significant differences with respect to the other resols. In chemical wood modification a direct correlation exists between the amount of resin (polymer) in the cell wall and the dimensional stability of the modified sample (Rowell 2005). Large oligomeric constituent and modification chemicals which are less polar lead to a lower degree of bulking and thus to lower dimensional stability of the modified samples. This occurs because these constituents are not able to form a stable network within the wood cell wall.

CONCLUSIONS

Organic oils extracted from lignin represent a potential source for aromatic compounds. If, in addition to the PF-resols, comparable resols from organic oils are to be synthesized, then a systematic fractionizing is an absolute necessity due to the heterogeneity of the organic oils. Based on the findings concerning the aromatic compounds investigated in this study, the fractionizing must be carried out in accordance with the following prerequisite: Phenol, o-, m- and p-cresol, guaiacol, and 4-ethylphenol, as typical mono-aromatic cleavage products of lignin, must be separated from the other products. Despite differences in the functionalities of their aromatic compounds, it is possible to synthesize organic resols from the aforementioned lignin products which, regardless of the type of network (linear or 3-dimensional), display no significant differences to the PF-resins with regard to chemical wood modification. In future studies emphasis needs to be placed on optimizing the yield of usable aromatics and their systematic fractionizing. Only through optimization can the potential for lignin products on an industrial level be realized.

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A new method of wood protection by chemical modification with polyglycerol succinate copolymer

Clément L'Hostis[1] , Emmanuel Fredon[1], Marie France Thevenon[2],
Philippe Gérardin[1]

[1]LERMAB, EA 4370, Université de Lorraine, Faculté des Sciences et Technologies, BP 70 239, F-54506
Vandœuvre-lès-Nancy, France. [email:emmanuel.fredon@univ-lorraine.fr]
[2]CIRAD, UR BIOWooEB, TA B-114/16, 73 Rue Jean-François Breton, F-34398 Montpellier CEDEX 5,
France[email: marie-france.thevenon@cirad.fr]

Keywords: Beech, dimensional stability, leaching, polyglycerol succinate, decay resistance

ABSTRACT

This paper deals with an original and non ecotoxic chemical treatment consisting in a vacuum /pressure impregnation step of wood with a water-borne prepolymer made from condensation of succinic anhydride (SA) and glycerol (G). Impregnated wood is then cured in order to induce *in situ* polymerization of the prepolymer (GSA) in the wood cell walls, giving thermoset polyglycerol succinate (PGS). Varying treatments conditions have been investigated in function of SA/G molar ratio, duration (6h to 72h), and curing temperature (103°C to 160°C). ATR-MIR spectroscopy provides confirmation of ester formation, whose intensity is temperature dependent. Weight Percent Gains (WPG) range between 40 and 55%, and decrease with curing temperature. Leaching resistance (LR) has been found strongly dependent to SA/G ratio: lowest LRs was achieved when SA/G molar ratio was fixed at least at 1.5, that seems to corresponds to PGS gelation, forming an insoluble network in the cell walls. LR is also closely dependent on temperature and duration treatment, and can decrease down to 0% according to the severity of curing conditions (160°C, 24h). Anti-Swelling Efficiency (ASE) of the treatment is also temperature dependent and reaches 64% at 160°C. Decay resistances of PGS treated wood against *C. versicolor and C. puteana* are also strongly temperature and time dependent. Mass losses (ML) are reduced to below 3% as soon as 160°C curing conditions are applied, that meet EN 113 standard requirements

INTRODUCTION

Wood is susceptible to dimensional instability and low durability due to water sorption processes. Wood modifications methods are targeted to overcome these drawbacks in wood service life for outdoor applications. Beyond them, chemical treatments have been extensively studied during last decades, succeeding to a couple of main industrial implementations, Accoya® and Kebony® (Rowell 2014, Lande *et al.* 2004). Many works are still devoted to alternative methods operating according to a two-stage process: a first step of wood impregnation with chemicals and a second step of curing at a moderate temperature (120-160°C) in order to activate the chemical reaction and fix the product in the wood (Sandberg et al. 2017, Despot *et al.* 2008, Noel *et al.* 2001).

Over the last decade, the development of bio-based chemicals, driven by the concern on the reduction of non-renewable petroleum resources is growing (Zia *et al.* 2016). Among many new bio-based monomers, succinic acid is a new platform molecule obtained by fermentation pathways and used for polybutylene succinate (PBS) synthesis (Jiang *et al.* 2017). Notably, bio-polyesters are synthetized for biomedical, packaging, coating uses. Glycerol is also a platform molecule that is the main byproduct of biodiesel industry (Okoye and Hammed 2016). Pure glycerol was used in polycondensation reactions to elastomeric polyesters (Li *et al.* 2013), or dendrimetric polymers (Zhang *et al.* 2014). There is still scarce study concerning the synthesis of polyesters from succinic acid and glycerol. Agach *et al.* (2012) showed the good stability and non ecotoxicity of polyesters from bio-based SA and G. For their part, Valerio *et al.* (2015) synthetized and characterized polyesters from crude glycerol and SA.

In the continuation of previous works lead in our laboratory concerning the polymerization in-situ of biobased polyesters in order to treat beech wood (L'Hostis *et al.* 2018, Noël *et al.* 2009), the paper deals with wood treatment with polyglycerol succinate (PGS) formed in-situ after impregnation of starting monomers. The choice of beech (*fagus sylvatica*) as wood substrate is justified as this species is limited in its uses from low durability and unstability for outdoor applications. Moreover this is a very abundant species in Lorraine, and significant improvement of its properties could promote new valorizations in construction area. We present in this paper the method developed for treating wood, and the validation results that were obtained: mass gain, dimensional stability, resistance to leaching, resistance to decay.

EXPERIMENTAL

Material Preparation

All the samples were Beech wood (*Fagus sylvatica*). Untreated quarter sawn planks conditioned at 20°C, 65% Relative Humidity (RH) were cut to reach the dimensions requested for each test. Prior to any treatment, the samples were oven-dried at 103°C until anhydrous state, and weighed (m_1).
Succinic anhydride (>99% m/m) was purchased from Acros Organics (Geel, Belgium). Glycerol (bi-distillated, 99.5% m/m) was purchased from VWR Chemicals (Leuven, Belgium). All chemicals were used without any further purification.

Treatment processes

Pre-polymer of succinic anhydride (SA) and glycerol (G) was obtained by mixing and heating the mixture under stirring at 130°C for 15 minutes and then cooled at 20°C. Excepted for one series of experiments, SA/G molar ratio was fixed at 1.5. Impregnation solutions were prepared by mixing the GSA pre-polymer to distilled water under stirring at 20°C until complete solubilization.
A batch of five native beech replicates has been prepared for each variant (formulation and curing conditions) and for each test. Each batch was impregnated with a dedicated solution under vacuum (20 minutes at 0.01 MPa) and pressure (60 minutes at 1 MPa). Samples were weighed after impregnation (m_2), and cured for different durations at the different temperatures (103, 120, 140 or 160°C), and weighed again to obtain their anhydrous mass after treatment (m_3). The Impregnation Rate (ImpR), Weight Percent Gain (WPG) were then calculated following in (Eqn. 1) and (Eqn. 2) respectively.

$$ImpR = \frac{m2-m1}{m1} \times 100 \tag{1}$$

$$WPG = \frac{m3-m1}{m1} \times 100 \tag{2}$$

Leaching Resistance

The 25x15x5 mm^3 samples were soaked individually in flasks with 20 mL of distilled water. The flasks were then placed on a shaking table at about 120 rounds per minute at 20°C. The water was changed at the end of cycles of 1, 2, 4, 8 and 16 hours according to the guidelines of the NF X 41-568 (2014) standard. Then, samples were oven-dried at 103°C until anhydrous state, and weighed (m_4). Leaching Rate (LR) was calculated according to the following formula (Eqn. 3):

$$\text{LR} = \frac{m3-m4}{m3-m1} \times 100 \qquad (3)$$

Decay Resistance

After EN 84 leaching procedure, 50x25x15 mm^3 treated samples, as well as beech controls, were gamma ray sterilized prior to biological tests. The samples were exposed to *Coriolus versicolor* (CV/0213/4) and *Coniophora puteana* (CP/0512/3) according to the EN 113 standard. Samples (both treated and untreated) were introduced in the culture flasks, and put on a grid to avoid waterlogging. Virulence controls were put in flasks in absence of treated samples. The samples were kept for 16 weeks at 22°C, 65% RH. After 16 weeks, the samples were cleaned, weighed (m_5) and dried at 103°C until constant mass (m_6).
Treated samples mass loss (%) was determined according to (Eqn. 4), and control samples mass loss (%) after (Eqn. 5):

$$Mass\ loss\ \% = \frac{m4-m6}{m4} \times 100 \qquad (4)$$

$$\text{Control Mass loss \%} = \frac{m1-m6}{m1} \times 100 \qquad (5)$$

Anti-Swelling Efficiency

For each treatment studied and controls, five 20x20x20 mm^3 samples have been soaked in distilled water for 24 hours, after 20 minutes under vacuum (0.01 MPa), to reach a relative humidity above the fiber's saturation point (FSP). The samples were measured in each direction using a measuring column at ± 0.01 mm. Afterwards, they were placed at 103°C, until anhydrous state was reached, to allow the measurement of anhydrous dimensions. The swelling of the samples was calculated according to Eqn. 6 and Anti-Swelling Efficiency (ASE) was defined as shown by the following equation Eqn. 7.

$$Swelling\ \% = \frac{Volume\ of samples\ above\ FSP - Volume\ of anhydrous\ samples}{Volume\ of anhydrous\ samples} \times 100 \qquad (6)$$

$$ASE = \frac{Swelling of treated wood - Swelling of control samples}{Swelling of control samples} \times 100 \qquad (7)$$

Attenuated Total Reflectance – Middle Infrared Spectroscopy (ATR-MIR)

All spectra were acquired with a Perkin Elmer Frontier spectrometer equipped with an ATR-MIR device. For polymer analysis, 10 grams of GSA solution were put in aluminum tray in oven at 160°C for 72 hours to reach polymerization, leading to a yellowish stiff resin. Thin layers of treated or untreated wood samples (<1mm), were obtained by splitting the 20x20x20 mm^3 blocks. Each sample was analyzed directly on the crystal of the apparatus. Each spectrum is an average of 4 samples spectra acquired with a resolution of 4 cm^{-1} after baseline correction and normalization after minimum and maximum value under absorbance axis using the dedicated Spectrum 10 software.

RESULTS AND DISCUSSION

Mass gain

The data concerning the impregnation rate (ImpR) and weight percent gain (WPG) are shown in Table 1 for the 20x15x5 mm3 samples cured during 72h at various temperatures. ImpR values (about 100% or over) prove a strong impregnation of the solutions into wood samples. WPG decreases with the increase of temperature, what is particularly noticeable at 160°C, and should result mainly from wood thermal degradation.

Table 11 : ImpR and WPG results for 25x15x5 mm3 samples

Heating temperature [°C]	**ImpR [%m/m]**	**WPG [%m/m]**
103	138.3 +/- 10.5	53.6 +/- 4.3
120	139.2 +/- 8.5	51.7 +/- 2.8
140	134.8 +/- 9.9	46.5 +/- 2.7
160	129.2 +/- 10.2	39.1 +/- 2.9

ATR-MIR spectroscopy

On figure 1, Spectra of treated beech samples compared to controls clearly show a strong increase of ester bands (C=O, 1735 cm^{-1} and C-O, 1188 cm^{-1}). Formation of ester functions can be attributed to the formation in wood cells of PGS chains from the condensation of glycerol hydroxyl function onto succinic acid. However, occurrence of wood grafting mechanism, due to the formation of ester linkage between wood hydroxyl functions and acidic terminal units cannot be excluded, as it was already underlined by L'Hostis *et al.* (2018). But such grafting should proceed by ester links that cannot be distinguished from ester bonds of polymers. It is noticeable that peaks intensity increases with heating treatment, traducing more intensive esterification.

Anti-Swelling Efficiency (ASE)

As seen in figure 2 (left side), dimensional stability of the samples is significantly improved by the treatment, with about 60% gain in dimensional stabilization at 160°C. However, a simple thermal treatment is known to improve wood stabilization. Comparing the results with wood controls subjected to only thermal treatment (fig 2, right), a significant difference is observed. It can be pointed out that the increasing ASE

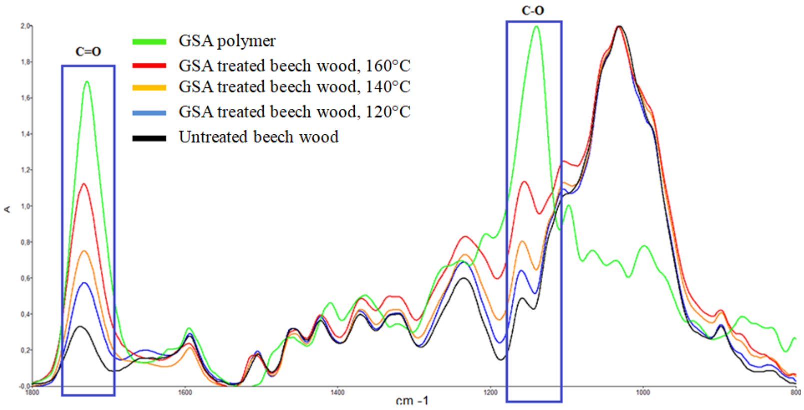

Figure 2: ATR-MIR spectra of samples treated by GSA at different temperatures, GSA polymer alone and untreated wood as controls

with heating temperature is well correlated with the increase in ester bands as shown with ATR-MIR data. These ASE results are comparable to previous ones obtained with citric acid/glycerol and tartaric acid/glycerol treated wood (L'Hostis *et al.* 2018).

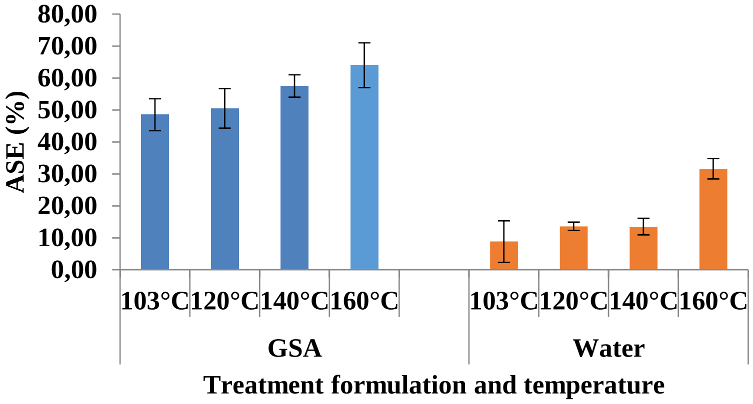

Figure 3: ASE(%) for GSA and water treated samples at different temperatures

Resistance to leaching

This criterion is of major importance: if chemicals are not correctly fixed, they would leach out during the service life of modified wood, the efficiency of the treatment would decrease and the product rejected in environment causing pollution impact.

Influence of monomers molar ratio

The polymer size and topology plays a major role in its retention in wood. Furthermore, it is well known that these properties are closely related to the molar ratio of monomers. Assuming that SA and G functionality are respectively 2 and 3, leaching rates were investigated in function of COOH/OH molar ratio. When treatments are conducted at 103°C, during 72h, results clearly show that LR is decreased when increasing COOH/OH ratio (figure 3). For the lowest COOH/OH ratio, LR can reach more than 60%, showing chemicals are not fixed. Agach et al. (2012) have already shown that gelation of GSA polymers occurs when COOH/OH ratio stands in a range 0,5 to 2 at full conversion of the reactant in defaults. It can be assumed that the fixation of GSA in wood can be explained by the gelation of the polymer. This assumption would be in accordance with negative solubility tests that were performed on GSA polymers, as gelation makes a polymer insoluble. This is the reason why, in the rest of the study, COOH/OH molar ratio was fixed at 1.0 (corresponding to SA/G molar ratio of 1.5).

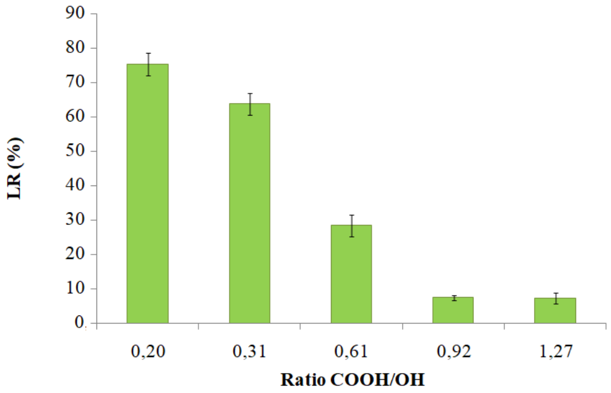

Figure 3: LR(%) in function of COOH/OH molar ratio

Influence of heating temperature and duration of treatment on LR

Keeping always 72h duration, it was found that LR dramatically fell down to 2% or less when heating treatment was driven to 120°C, 140 or 160°C. In order to verify the feasibility of the treatment in conditions that can fit with industrial requirements, the heating duration of treatment was shortened (6h, 10h, 24h). The temperature of 103°C was not chosen in reason with unsatisfying leaching results compared to higher temperature, limiting the range of temperature between 120°C and 160°C. Leaching results are plotted in the figure 4. Results clearly show that heating temperature has great influence on leaching rate: since 120°C, LR is severely reduced, and LR is closed to 0 for 140 and 160°C treatments. Duration plays a major role in the fixation of chemicals: especially for low temperature treatments, strong variations of leaching rate were observed, starting from 20% LR when conducted during 6h down to 5% for 24h at 120°C. However, when conducted at higher temperature, (140°C and 160°C), LR variations are weaker.

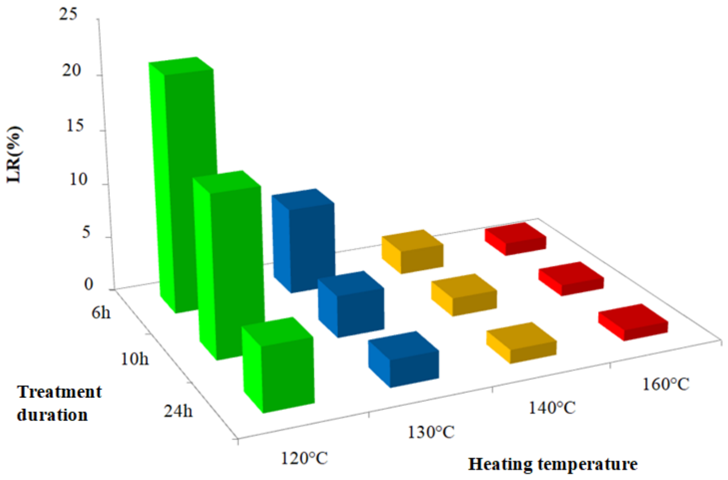

Figure 4: LR (%) in function of treatment duration and heating temperature

Decay resistance:

As shown in figure 5, decay resistance of PGS treated wood strongly depends on curing temperature and duration. Mass losses (ML) are reduced to below 3% if 160°C is applied. Control samples placed in the same flasks as the treated samples showed a significant degradation (always over 20% ML), likewise the virulence control, proving that the fungus in the test was discriminant enough, and that the treatment is effective against *C. versicolor and C. puteana*. ML are low enough to satisfy EN 113 standard requirements when curing temperature is sufficient.

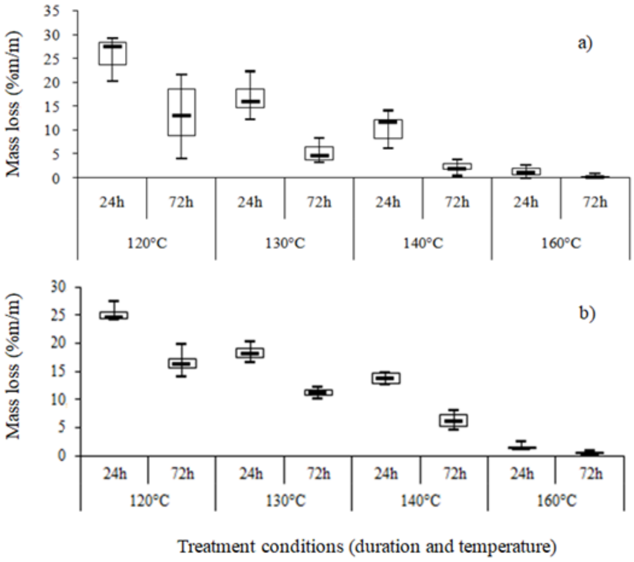

Figure 5: mass losses after degradation of GSA treated samples by Coriolus versicolor a) and Coniophora puteana b)

CONCLUSION

Increasing heating and duration treatment leads to better fixation of the product in wood cell walls, better dimensional stabilization, better leaching rate and decay resistance. The best compromise was obtained at 160°C during 24h, with 1.5 SA/G molar ratio. ATR-MIR measurements confirm the impact of temperature in the formation of ester bonds. Moreover, optimal molar ratio avoiding severe leaching seems to correspond to conditions of gelation giving insoluble PGS copolymer. It has been pointed out that grafting of carboxylic end groups on wood hydroxyl functions may also participate to the achievement of conferred properties.

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The effect of humidity and temperature on the dynamic-mechanical behaviour of phenol-formaldehyde impregnated beech wood veneer

Leo Felix Munier[1], Tom Franke[2], Nadine Herold[3], Alexander Pfriem[4]

[1]HNEE, Schicklerstr.5, D-16225, Eberswalde [email: leofelix.munier@hnee.de]
[2]BFH, Soluthurnstrasse 102, CH-2504, Biel [email: tom.franke@bfh.ch]
[3]HNEE, Schicklerstr.5, D-16225, Eberswalde [email: nadine.herold@hnee.de]
[4]HNEE, Schicklerstr.5, D-16225, Eberswalde [email: alexander.pfriem@hnee.de]

Keywords: DMTA, humidity sweep, phenol-formaldehyde, temperature sweep, veneer softening

ABSTRACT

Within the present pilot study, dynamic-mechanical thermal analyses (DMTA) measurements were conducted to verify the applicability of DMTA measurements for the investigation of beech veneer (*Fagus sylvatica* L.) softening induced by phenol-formaldehyde (PF) impregnation, temperature and humidity. Analyses were performed with a DMTA equipped with a humidity generator. The samples were subjected to dynamic tensile load in radial direction with a sinusoidal oscillation of 1 Hz. The storage modulus (E') and the loss factor ($tan\delta$) of the uncured PF impregnated and the untreated control veneers were assessed firstly for an increasing temperature and secondly for an increasing humidity. The results are very promising and approve DMTA to be a valuable technique to assess the softening of wood veneer. In particular, findings evince a reduction of the normalized storage modulus with increasing humidity indicating an increasing plasticization of the samples due to moisture. Similar effects were found with an increasing temperature. These effects are more distinct for samples impregnated PF than for the control specimens. Especially the temperature induced-softening differs markedly for the PF impregnated compared to the reference samples.

INTRODUCTION

The present results are obtained from preliminary DMTA analyses which are part of a sequence of investigations working on PF modification of European beech veneer for moulding applications. As moulding of wood corresponds considerably with wood flexibilization or wood plasticization, the study has been carried out to describe the effects of humidity, temperature, and PF impregnation on the softening behaviour of beech veneer assessed by DMTA measurements using a DMTA equipped with a humidity chamber.

Known flexibilization approaches can be distinguished into hydromechanical, chemical, enzymatic, and hygrothermal flexibilization (Heymann 2010). Besides, the use of additional layers can also promote a greater bending.

Among those different approaches, the probably most common treatments consider a hygrothermal flexibilization which affects a cell wall softening by increased humidity and temperature. This effect is reversible since all main wood components remain almost unchanged and cell walls are softened only for the moment of processing allowing a temporary bending and shaping of wood (e.g. Fuchs 1963). According to Nicholas (1973), steaming of wood is the most traditional and common processing among all hygrothermal treatments. Apart from temperature, various chemicals soften wood cell walls similar to water. This mechanism of cell wall softening is commonly referred to as plasticization.

Phenol-formaldehyde is commonly used in wood industry as adhesive, especially if the bonds require a resistance to heat and moisture. Besides, PF is also suitable for an impregnation of wood. The advantages of PF impregnated wood and wood veneers are the enhanced dimensional stability and the reduction of water absorption (Stamm and Seborg 1955, Gabrielli and Kamke 2010). However, PF is also suitable as plasticizer of wood veneer for moulding applications (Shams and Yano 2004) and as plasticizer to realize a densification of wood (Shams *et al.* 2004).

Most recently, Franke *et al.* (2018) investigated the two- and three-dimensional moulding behaviour of PF impregnated beech veneer samples. The obtained results evince a plasticization of wood by PF impregnation correlating with an enhanced mouldability of the samples. Especially those results from the cupping test displayed a greater mouldability by greater shaping paths compared to water-saturated samples. However, the PF for impregnation was a common water-based resol and thus, plasticizing effects cannot be solely attributed to the PF but rather to the mixture of PF and water.

The current study is a pilot study and a continuation of the previous work mentioned above. Non-destructive measurements employing a DMTA were performed to identify the impact of increased temperature on veneer softening. Furthermore, results from a humidity sweep provide information about the effect of humidity and moisture content of the PF impregnated samples on veneer softening.

EXPERIMENTAL

Veneers

The samples used for the investigations were made from beech wood veneer (*Fagus sylvatica* L.). As previously found, industrially manufactured veneers are unsuitable for DMTA measurements due to structural damages resulting from the manufacturing process. Furthermore, commercially available veneers have no defined anatomical orientation. For these reasons, the veneers used in the present study were produced manually with a defined anatomical orientation and even annual ring widths from a single board. Therefore, the board was first sawn into slices with standing annual rings (Fig. 1). Afterwards, those slices with a thickness of *appr.* 5 mm (tangential) were downsized with a wide-belt-sander to realize a thickness of 0.7 mm. Finally, samples were cut from those veneers with dimensions of 45 mm x 11 mm x 0.7 mm (radial R x longitudinal L x tangential T).

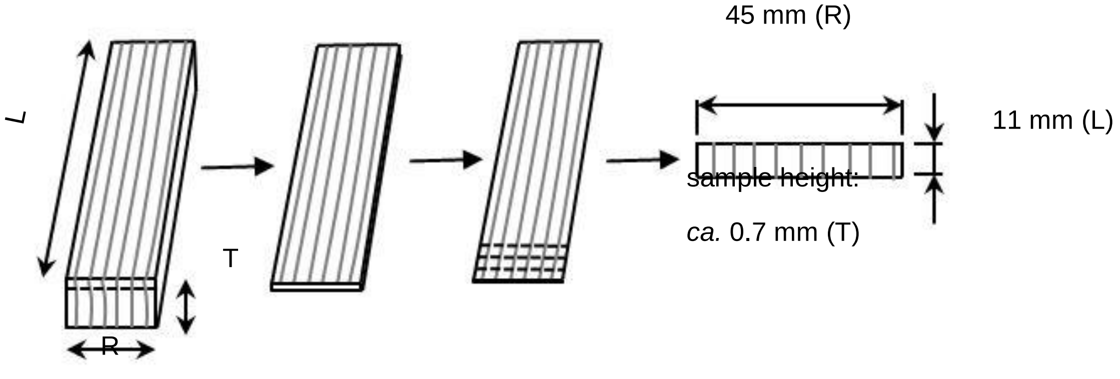

Figure 1: Schematic illustration of the sample preparation (L: longitudinal; R: radial; T: tangential).

Phenol-formaldehyde (PF)

For the present study, a commercially available water-based resol from Prefere Resins® GmbH, Erkner, Germany, was used for impregnation.

Impregnation

The beech wood veneers samples were dried to constant weight in a desiccator with silica gel prior to impregnation. Subsequently, the veneers were impregnated with PF in a desiccator under vacuum at -90 kPa for 24 hours. After impregnation, the veneers were pre-conditioned for the DMTA measurements in a climate chamber at 15% relative humidity and 25 °C for 24 hours. To reduce unintentional curing processes beforehand the DMTA measurements, each specimen was prepared individually and just in time.

DMTA

The DMTA measurements were performed with the DMTA “Eplexor® 25” from Gabo Qualimeter Testanlagen GmbH equipped with a humidity generator Hygromator® and tension clamps (Fig. 2). Each DMTA measurement was repeated on three specimens to ensure reproducible results.

Figure 2: DMTA device “Eplexor 25“ equipped with a humidity generator.

Temperature sweep

To identify the impact of temperature and PF impregnation on the softening of European beech veneer, DMTA analyses were conducted using a temperature sweep with a heating rate of 1 °C/min in a temperature range between 25 and 150 °C and a frequency of 10 Hz. The specimens were tested in radial direction in tensile mode with a clamp distance of 33 mm. A dynamical strain of 0.02% was chosen and a static load that exceeded the dynamic load by 100 to 150% during the experiment to prevent specimens from buckling. Results are shown as normalized storage modulus (E’) and loss factor ($tan\delta$). In order to prevent the clamps from soiling, both ends of the specimens were covered with temperature resistant foil (Exact Film 210 from Exact Plastics®).

Humidity sweep

Alike the samples in the temperature sweep, for the current study uncured samples were stressed dynamically in radial direction in tensile mode with a sinusoidal frequency of 1 Hz. The storage modulus (E') and the loss factor ($tan\delta$) of the uncured PF impregnated and the untreated control veneers were determined at a relative humidity of 15%, 60%, and 85% and a constant temperature of 25 °C. The clamp distance was set on 35 mm. All measurements were carried out with a dynamic strain of *appr*. 0.03% and a static strain of *appr*. 0.065%. Every measurement comprised 3 segments each with a different relative humidity (15%, 60%, and 85%). The segment-specific setting of relative humidity, temperature, soak-time, measuring time and number of measuring points are shown in Table 1. The soak-time of the first segment was chosen to be shorter because the impregnated samples were already pre-conditioned at 15% relative humidity and 25 °C for 24 hours.

Table 1: Segment-specific settings.

DMTA-segments	**Relative humidity [%]**	**Temperature [°C]**	**Soak-time [h]**	**Measuring time [h]**	**Measuring points**
1st segment	15	25	6	0.5	14
2nd segment	60	25	8	0.5	14
3rd segment	85	25	8	0.5	14

RESULTS AND DISCUSSION

The performed DMTA analyses seem to be a promising and revealing tool to get more information on the plasticizing effect of PF impregnated veneers and control specimens.

Figure 3 displays the results obtained from the temperature sweep. The control specimens show a slightly decreasing normalized storage modulus with increasing temperatures. In contrast, PF impregnation leads to a more pronounced decrease of the storage modulus until to *appr*. 106 °C corresponding with a softening of the sample. Above 106 °C, the storage modulus increases induced by the evaporation of water and the beginning polymerization of the PF.

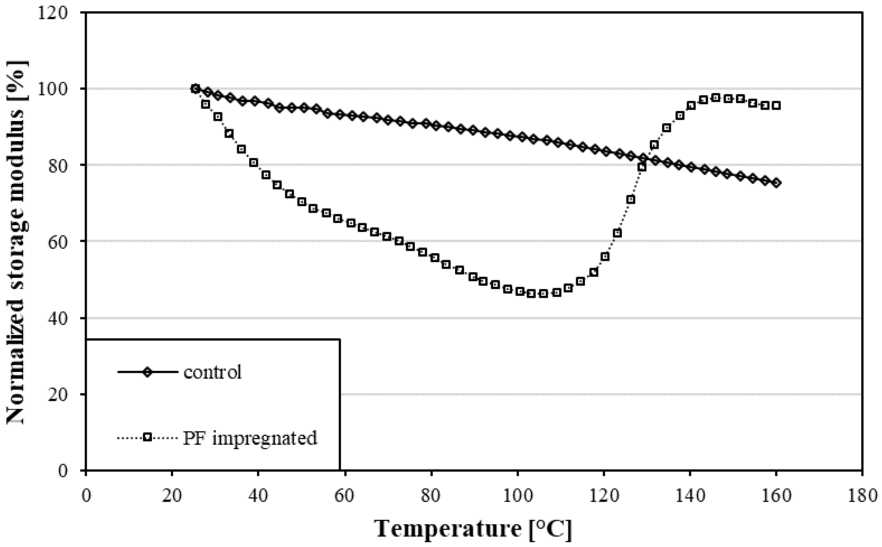

Figure 3: DMTA analyses. Results from a temperature sweep with a heating rate of 1 °C/min.

However, these results consider the temperature-induced behaviour of water-based PF impregnated specimens. In consequence, effects cannot be clearly allocated to be caused by water or PF.

Additional information on the effect of humidity on the dynamic-mechanical behaviour of PF impregnated specimens were achieved by DMTA measurements running a humidity sweep. Results displayed in Figure 4 evince an intensified softening behaviour of impregnated samples compared to untreated control specimens under any relative humidity.

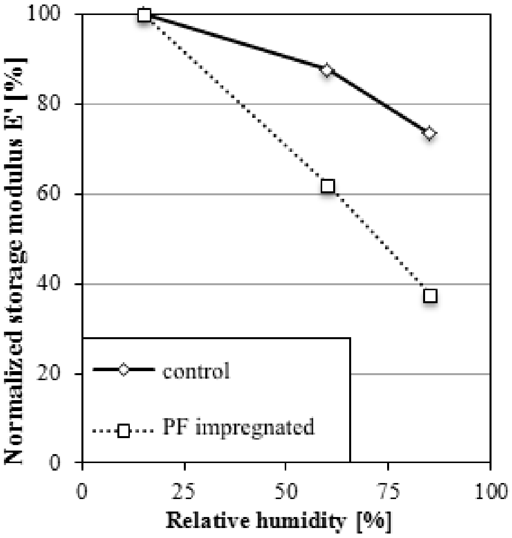

Figure 4: DMTA analyses. Results from a humidity sweep.

CONCLUSIONS

The gained pilot results are in good agreement with earlier findings from two- and three-dimensional moulding and substantiate the claim, that PF impregnation can be used to facilitate veneer plasticization and enhanced moulding. However, the present findings are preliminary results to verify particularly the applicability and reproducibility of DMTA measurements to determine wood softening due to impregnation, increasing temperature and humidity. Thus, the included results do not consider any additional characteristic of PF resins, such as molecular weight or solid content. Further studies will apply the found settings and parameter for material studies on impregnated veneers and will consider different PFs in order to determine the effect *e.g.* of solid content or molecular weight of the impregnation agent.

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Biopolyesters for wood modification: technical validation towards implementation

Marion Noël[1], Charlotte Grosse[1,2], Ingunn Burud[3], Marie-France Thévenon[4,5], Philippe Gérardin[2]

[1]Bern University of Applied Sciences; Department Wood, Architecture and Civil Engineering, Solothurnstrasse 102, 2500 Biel, Switzerland [email: marion.noel@bfh.ch, charlotte.grosse@bfh.ch]
[2]LERMaB, EA 4370, Université de Lorraine, Faculté des Sciences et Technologies, Vandoeuvre-lès-Nancy, France [email: philippe.gerardin@univ-lorraine.fr]
[3]Norwegian University of life sciences, Faculty of Science and Technology, Ås, Norway [email: ingunn.burud@nmbu.no]
[4]CIRAD, UR BIOWooEB, TA B-114/16, 73 rue Jean-François Breton, F-34398 Montpellier Cedex 5, France [email: marie-france.thevenon@cirad.fr]
[5]BIOWooEB, Univ. Montpellier, CIRAD, Montpellier, France [email: marie-france.thevenon@cirad.fr]

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ABSTRACT

Wood modification with bio-polyesters has been reported in terms of treatments synthesis, interaction between wood polymers and bio-polyesters, evaluation of the durability, leaching resistance and dimensional stability of treated wood. These investigations led to the selection of two variants. In view of industrial implementation, this article reports the mechanical characterization and process ability evaluation of wood modified accordingly.

INTRODUCTION

The original idea behind this research was to create a durable and sustainable new material, by association of bio-resources (namely wood and biopolymers). Unlike wood plastic composites combining wood fibres as reinforcement into a polymer matrix, the approach developed here was to impregnate the solid wood matrix with bio-based polymer(s) as reinforcement for performance improvement. The polymer choice inclined towards bio-polyesters as poly(lactic acid) (PLA), poly(glycolic acid) (PGA), poly(butylene succinate) (PBS) and poly(butylene adipate) (PBA) because of their bio-based character and their expected chemical affinity with wood. Inspired by standard procedures intensively described in wood modification literature, the developed method consisted in a 2-step treatment: impregnation of polymers precursors in wood under vacuum followed by heat treatment to initiate in-situ polymerization and potentially chemical grafting on wood. The impregnation step revealed to be easily carried out leading to significant weight uptake of precursors. The *in situ* polymerization was proven by gel permeation chromatography of extracted polymers. The final material consisted in slightly darkened modified wood with excellent biological resistance and dimensional stability (Noël 2010, 2015). Beech wood was the main species considered in this work, because being readily available in Europe and in need of performance increase to promote its use. The high volumetric variation coefficient and poor durability constitute the main limitations of this species, which is on the other hand easily impregnable. Some tests were also carried out on pine sapwood, fir and douglas fir. According to bio-polymers, many variants were considered over the years with varying objectives. For rheology and reactivity adjustment, PGA and PBA were evaluated as crude polymers for treatment, and as co-polymers. The following systems of oligomers were examined: PLA, PGA, and copolymers thereof (with varying ratios of monomers), PBS, PBA, and co-polymers thereof (with varying ratios of monomers) (Noël 2015, Vitkeviciute 2015, Noël *et al.* 2014, 2015). For compatibilization between wood and PLA, maleic anhydride was added to the treatment system (Grosse *et al.* 2016). To catalyse PLA treatments, additionally to thorough screening of usual catalyst of PLA polymerization (Noël 2010), citric and tartaric acids were also appraised separately. As polyacids, their addition into the mixture was expected to create ramifications in the oligomer chains. To increase durability, hydrolysable chestnut tannins were included in PLA mixtures (Grosse *et al.* 2016). Out of those combinations, best results were obtained with PLA and PBS, with which the process was developed and characterized further. Precursors were constituted of lactic acid monomers or short oligomers produced by polycondensation (OLA), and of PBS oligomers obtained by catalyzed pre-polymerization (OBS) of butan-1,4-diol and dimethylsuccinate. Viscous liquid, OLA diffused into wood under vacuum at room temperature, while OBS must be heated over melting temperature to penetrate wood structure. The treatment conditions revealed to be more influent than any additives mentioned above. For that reason, many optimization trials were carried out to define the most efficient parameters combination: treatment temperature, duration and relative humidity (Noël *et al.* 2016, Grosse *et al.* 2017, 2018). Besides, once most important properties validated, the implementation feasibility was investigated: efficiency of treatment wood at 12% and 30% equilibrium moisture content (EMC), impregnation of real scale wooden objects, elaboration of thermal treatment judicious cycle, … This article reports the global characterization of the most promising treatments elaborated within the framework of several R+D projects and exposes the first attempts of implementation in collaboration with the companies Corbat Holding SA (Glovelier (JU), Switzerland) and Jungbunzlauer AG (Headquarters in Basel, Switzerland).

EXPERIMENTAL

Wood treatment

LA treatment consisted in a commercial lactic acid water solution (88%). OLA-treatments consisted in oligomers of lactic acid obtained by limited polycondensation, with wide molecular mass distribution and degree of polymerization of 5 - 10. OBS-treatments consisted in oligomers of PBS obtained by polymerization of butan-1,4-diol and dimethyl succinate (catalyzed with titanium (IV) butoxide), with wide range of molecular mass distribution and degree of polymerization of 15 – 25 (full procedures in Noël *et al.* 2014).

Wood samples (beech, fir, douglas fir and pine) were treated either at 0%, 12% or 30% EMC. Depending on treatment, the impregnation was carried out under vacuum (0.015MPa) at room temperature (LA/OLA-based treatments) or 70-90°C (OBS-based treatments). After ca. 2h of impregnation (30min-alternation of vacuum and soaking), samples were either set on aluminium foil for thermal treatment in ventilated oven (LA/OLA-based treatments), or subjected to wet cycle in autoclave (100°C/100% relative humidity (RH) for 2h) beforehand (OBS-based treatments) (full procedures in Noël *et al.* 2014). Thermal treatment temperature and duration differed and are defined thereafter.

Mechanical evaluation

Bending modulus (MOE) was measured according to EN 408 (2010). The 4-point bending test was done on oriented samples (150 x 7 x 12 mm^3, L x R x T for all dimensions in the text). The largest deflection was measured at the samples mid-length by a deflection sensor (accuracy 0.02 mm). The MOE was calculated with Eqn. 1 between 0.1F$_{max}$ and 0.4F$_{max}$ (maximal force):

$$MOE = \frac{3al^2-4a^3}{2bh^3\left(2\frac{w_2-w_1}{F_2-F_1}-\frac{6a}{5Gbh}\right)} \quad \text{(MPa)} \qquad (1)$$

with a = spacing between one support and the closest load application point (mm); l = spacing between supports (mm); b = sample width (mm); h = sample height (mm); F_2 - F_1 = force increase on the regression line (N); w_2 - w_1 = deflection increase corresponding to ($F_2 - F_1$) (mm) and G = shearing modulus, defined as ∞ when not known (MPa).

Compression resistance was measured according to NF B51-007 (1985). The test was achieved on oriented samples (60 x 20 x 20 mm^3, L x R x T). Prior to testing, samples were stabilized at 12% EMC. Axial compression strength was calculated with Eqn. 2:

$$C_H = \frac{P}{ab} \text{ (MPa)} \qquad (2)$$

with P = maximal force (N) and ab = sample section (mm^2).

A comparative approach of wood shearing strength of treated and untreated wood was carried out by applying tensile force on samples prepared according to the EN 302-1 (2013), normally dedicated to adhesive evaluation. Samples were not glued. Two grooves were cut on each side of solid samples (110 x 12 x 24 mm^3), deep to the same wood plan, defining the area submitted to shearing force. Shear strength was calculated with Eqn. 3:

$$f_v = \frac{F_{max}}{A} \text{ (MPa)} \qquad (3)$$

with Fmax = breaking force (N) and A = glued surface (mm^2).

Process ability

Cutting tools wear

For each treatment variant, a new blade was used to produce 3.4 km of wood chips (samples dimensions: 600 x 50 x 40 mm^3). Blades were used on one half of their length; the other half constituted the reference. Wood samples were milled in length as shown in Figure 1. Blade's wear was measured with scanning electron microscope (SEM), positioned as shown in Figure 2. Micrographs were taken after generation of 0.5, 1.6 and 3.4 km. Each micrograph was scaled and exhibited measurements of the edge recession.

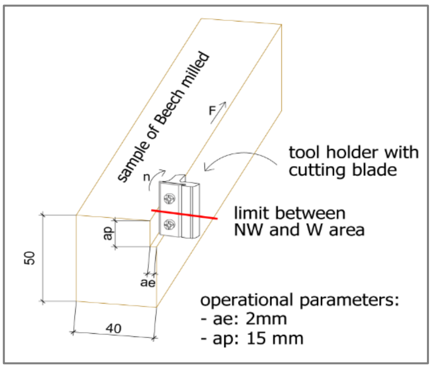

Figure 1: Description of milling parameters. W : worn, NW : non worn sections (Ruberu Q.)

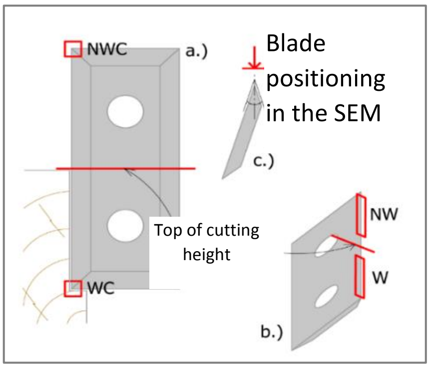

Figure 2: Description of milling parameters. WC : worn, NWC : non worn corners (Ruberu Q.)

Gluing

The longitudinal tensile shear strength was evaluated according to the procedure described in the standard EN 302-1 (2013). The test was carried out on oriented samples (110 x {2 x 6 + glue line} x 24 mm^3). Samples gluing was achieved with one-component polyurethane resin Collano RP 2710 (200 $g.m^{-2}$ on one side), under 0.8 MPa for 5h. After gluing, samples were stored for one week at 20°C/65%RH. Shear strength was calculated with Eqn 3.

Coating

Wood samples were planed, sanded and stabilized at 20°C/65% RH before spray gun application of a 2-layer acrylate coating (Aquaprotect, Feyco Treffert) for a total wet thickness of 100 $g.m^{-2}$ each. Coated samples were stored at 20°C/65% RH until weight stabilization before conducting pull-off adhesion test (EN ISO 4624 (2016)). Adhesion strength was calculated with Eqn. 4. The nature of failure was always observed and described.

$$\sigma = \frac{F}{A} \text{ (MPa)} \qquad (4)$$

with F = breaking force (N) and A = the dolly area (mm^2).

RESULTS AND DISCUSSION

Optimization of treatments and treatment conditions

LA/OLA based treatments

The addition of catalysts into lactic acid monomers and oligomers before *in situ* polymerization was never beneficial, leading to strong degradation of the material (observed with 0.6% of sulfuric acid, or 5% of tin octoate a.o., Noël 2010) or no significant effect on wood physical properties (citric and tartaric acid). For compatibilization, maleic anhydride (MA) conferred resistance to water leaching similar at high and low treatment temperature, but this improvement was not substantial enough to compensate the non-renewable nor non-environmentally friendliness of MA (Grosse *et al.* 2016). The addition of hydrolysable chestnut tannins (TH) lead to biological resistance similar at high and low treatment temperature, but this improvement was not substantial enough to compensate the increase in wood hygroscopicity resulting from TH addition, even with tannins acetylated prior to *in situ* polymerization (Grosse *et al.* 2016). The pre-polymerization of LA was expected to promote the extent of *in situ* polymerization, and to pre-evaporate the water contained in the commercial aqueous solution. However, LA aqueous solution without any prior preparation conferred similar final performance. The resulting decisive parameters for performance improvement with LA treatment (dimensional stability, fixation in wood and durability) were the treatment temperature (threshold at 160°C) and duration (threshold not defined yet), even though this selection is only valid for anhydrous, small dimension samples.

OBS based treatments

The OBS oligomers were made of longer chains, unable to diffuse into wood cell wall during thermal treatment. However, it was observed that carrying out wet thermal treatment induced cell wall swelling by water vapour leading to polymers partial diffusion in wood ultra-structure. That procedure appeared to be the most efficient procedure for dimensional stabilization of wood. It resulted that the decisive parameters for performance improvement (dimensional stability, fixation in wood and durability) were defined after impregnation as a first wet step at 100°C/100% RH for 2h, followed by drying at 120°C for 48h, even though this selection is only valid for anhydrous, small dimension samples. OBS oligomers did not show any significant further *in situ* polymerization even at high temperature (160°C). For that reason, the attention focused on good diffusion and fixation in the cell wall (Noël 2015, Noël *et al.* 2016, Grosse *et al.* 2017).

Mechanical performance

Given that the mechanical characterization was carried out on small no defect samples, a complete evaluation on bigger dimensions is still under investigation. However, the data below allowed the pre-evaluation of the up-scaling potentiality.

Two distinct mechanical behaviours were revealed depending on the bio-polymer constituted into wood and its interaction with the lignocellulosic matrix.

As thermal treatment makes LA or OLA diffuse into the cell wall and polymerize *in situ*, leaving lumens free, mechanical resistance and material elasticity were impacted. While bending and compression resistance increased because of polymer reinforcing action in wood, the elasticity decreased slightly resulting in stiffer material (Figures 3, 4, 5). Treatment acidity combined with high temperature leads to simultaneous weakening of wood internal cohesion, measured by shearing strength significant decrease (Figure 6). Final application of LA/OLA-treated wood must be wisely designed.

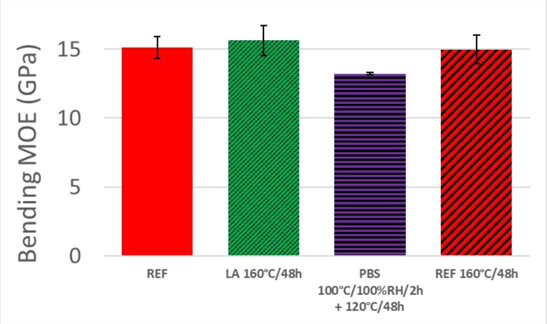

Figure 3: MOE of treated wood in comparison to references

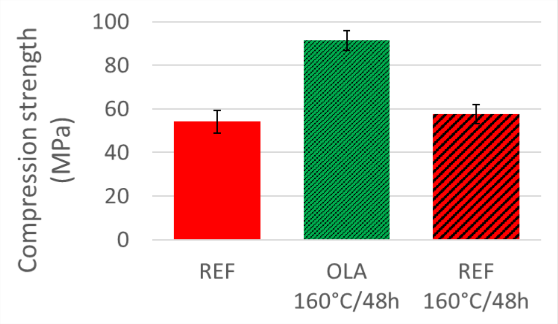

Figure 4: compression strength of treated wood in comparison to references

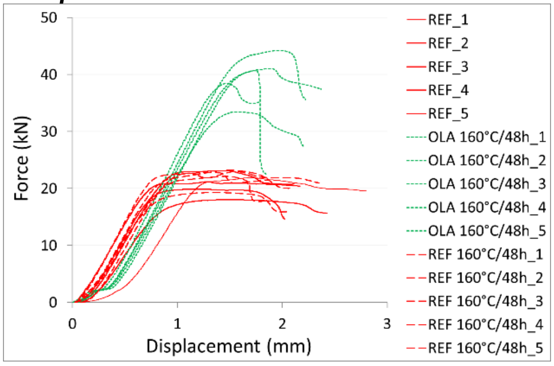

Figure 5: force/displacement curve of samples subjected to axial compression force

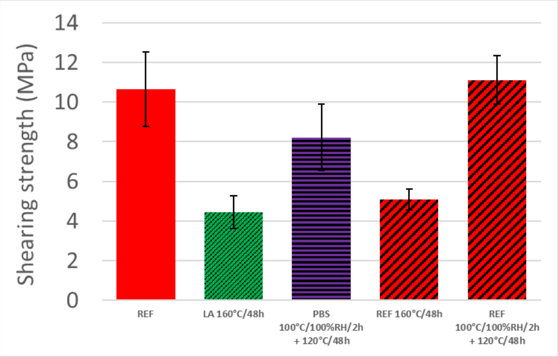

Figure 6: shearing strength of treated wood in comparison to references

Although not reported here, it was observed that thermal treatment of LA/OLA treated wood could be achieved at either 140°C or 160°C without any significant effect on final mechanical properties. The addition of TH did not show any significant impact either. Co-polymerization of LA and GA did not lead to any significant difference either. With only partial diffusion into the cell wall and filling of pores mostly, OBS treatment did not show significant influence on mechanical properties. The impact on wood internal cohesion was also limited, with slight shearing strength decrease observed (Figures 3, 4, 6). Together with very good durability and dimensional stability, OBS treatment gave better promises, mechanically wise, than LA/OLA treatments. Mechanical properties of treated wood (either LA/OLA or OBS) seem to be of interest for selected applications, especially in comparison to thermally treated wood, known to lose mechanical resistance during the process (Esteves and Pereira 2009). Thermally treated under relatively soft conditions in comparison to most industrial procedures (160°C/48h/0%RH), thermo-treated references produced in the lab (REF 160°C/48h) showed no loss of strength in bending nor in compression in comparison to the untreated controls. However, the impact on fibres cohesion was significant.

Process ability

Cutting tools wear

Wood treatments increased wood density and material acidity significantly. *In situ* polymers might also lead to higher cutting tools fouling. Quantification of the influence of treatment on cutting tool wear was therefore necessary before implementation attempt.

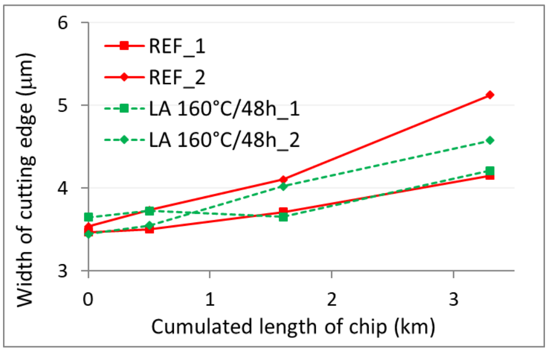

Figure 7: Growth of edge with cumulated length of chip created.

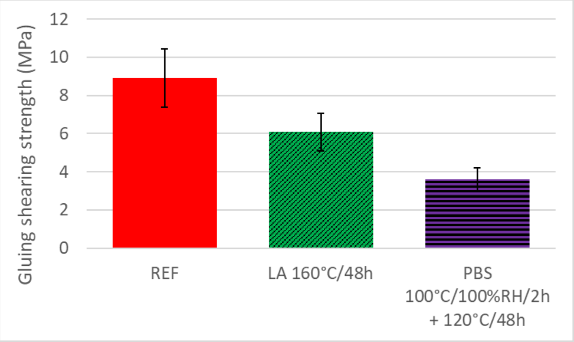

Figure 8: Gluing shearing strength of wood reference and wood treated (LA – PBS)

It was shown that the LA led to similar pattern to controls (Figure 7). There was no significant increase in cutting tools wear observed (variations due to measurement accuracy). The test must however be done with OBS treated samples, that might demonstrate bigger influence, not necessarily on tools wear but rather on tools clogging.

Gluing

Figure 8 reports the substantial influence of treatments on gluing resistance with usual polyurethane adhesive for structural applications. The acidity of LA treatment and the lumen filling with OBS polymers were the likely explanations of the significant decrease in gluing performance. More investigation must be carried out on this matter to determine the definitive feasibility of gluing: wood preparation, type of adhesive,… However, because dimensional stability of wood was increased by treatment, the lesser stress applied on wood assemblies in use should be taken into consideration.

Coating

The nature of failure of reference samples (heated or not) corresponds mainly to adhesive failure between substrate and first coat. The influence of temperature was indicated by higher proportion of cohesive failure in the substrate (REF 160°C/48h) linked to lower adhesive strength. Nature of failure of LA treated samples corresponds mainly to cohesive failure of substrate with similar decrease in adhesive strength as observed on heated references (REF 160°C/48h). This would mean a slightly better adhesion (nature of failure) coupled with impact on material resistance (adhesive strength). Nature of failure of OBS treated samples was 100% adhesive failure between substrate and first coat with significantly lower adhesive strength than other samples.

This shows a clear incompatibility between coating and OBS oligomers on samples surface. Not reported here, the inclusion of TH had no substantial effect on coating adhesion properties, nor the pre-polymerization of LA before treatment (Figure 9).

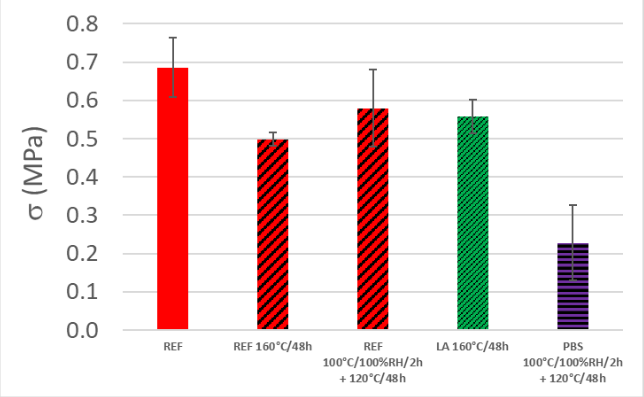

Figure 9: Adhesion strength of coating

Implementation

The industrial implementation of LA and OBS implies that treatment must be possible on wet wood (EMC higher than fiber saturation point for some applications) and good diffusion in real scale products must be feasible. Besides, treatment conditions must be in accordance with productivity concerns. Despite the product acidity, LA formulation storage and impregnation seem to be feasible. The raw material is readily available and aqueous solutions diffuse properly in wood. However, conducting thermal treatment at 160°C on wet wood is hardly possible without causing deleterious defects on wood pieces due to stress relaxation. Unfortunately, water and high temperature are logically preventing polycondensation of LA *in situ* (Grosse *et al.* 2018). First real scale investigations were carried out for railway sleepers treatment in industrial wood thermo-treatment facilities (Corbat Holding SA, Switzerland). A 48h thermal treatment cycle was carried out starting with 12h ramp to reach 180°C / 20% RH followed by 36h maintaining these conditions. The cracks on raw pieces were drastically enlarged by the treatment process. The current work carried out consists in defining a suitable thermal treatment cycle with wise combination of temperature and relative humidity, leading to no wood performance decrease. In the OBS case, handling treatment of wet wood might be beneficial to polymer diffusion. Impregnation at 70-90°C is feasible as well. The most limiting parameter is raw material supply. Heat initiated reaction of butan-1,4-diol and dimethylsuccinate, non-miscible liquids, directly in wood, was never attempted but seems hardly feasible. There is a necessary pre-polymerization step that would have significant impact on economic viability due to investment/sub-contracting cost. This kind of treatment appears to be non-economically viable for the time being for usual applications in wood construction sector.

CONCLUSIONS

LA/OLA and OBS treatments have shown many promising effects on wood, especially in terms of durability and dimensional stability (weight loss according to EN113, exposure to *Coriolus versicolor* and *Coniophora puteana* < 3% and anti-swelling efficiency (ASE) > 65% for LA/OLA; weight loss according to accelerated screening test, exposure to *Coriolus versicolor* ≈ 2%, 3.7% according to EN113 and ASE ≈ 60% for OBS). Leaching values due to exposure to water were also very acceptable (< 2% according to NF X 41-568 (2014) for OLA). Besides, durability tests revealed the absence of mould attack, and OBS treated wood kept very attractive appearance and homogeneous colour change after 24 months of exposure. Further investigation via hyperspectral imaging of weathered samples revealed a different ageing pattern of OBS-treated samples in comparison to references and OLA modified wood.

Most chemical modification processes lead to wood structure weakening because of the influence of treatment on wood ultra-structure. LA/OLA treatments impacted wood fibers connection, while OBS treatments made gluing particularly challenging. If specific attention must be given to a wise application design, the general performance of LA/OLA and OBS treatments seems competitive with current commercial technologies. Their implementation would widen the bio-modified wood offer on the market.

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The Maillard reaction for wood modification: The influence of reagent concentrations, reaction temperature and soaking time on the leachability and cell wall penetration of reagents

Kelly Peeters[1,] Andreja Kutnar[2], Črtomir Tavzes[2], Jaka Pečnik[3] and
Callum A.S. Hill[4]

[1]InnoRenew CoE, Livade 6, SI-6310, Izola [email: kelly.peeters@innorenew.eu]

[2]InnoRenew CoE, Livade 6, SI-6310, Izola *and* University of Primorska, Andrej Marušič Institute, Muzejski trg 2, SI-6000, Koper [email: andreja.kutnar@innorenew.eu; crtomir.tavzes@innorenew.eu]
[3]University of Primorska, Andrej Marušič Institute, Muzejski trg 2, SI-6000, Koper [email: jaka.pecnik@iam.upr.si]
[4]InnoRenew CoE, Livade 6, SI-6310, Izola and Norwegian Institute of Bioeconomy Research (NIBIO), Pb 115, NO-1431, Ås [email: enquiries@jchindustrial.co.uk]

Keywords: beech, pine, leachability, Maillard reaction, wood modification

ABSTRACT

Finding efficient ways to decrease wood decay caused by fungi and increasing its dimensional stability is an important issue in timber construction and other applications. A possible way to avoid wood decay by fungi and increase its dimensional stability, is by reducing the water content of wood. Water is a primary condition for fungal growth and induces shrinking or swelling in wood. By bulking the wood cell walls with chemical reagents, the space where water normally occurs gets occupied. For effective protection using impregnation modification, it is a requirement that the bulking agent is located mainly in the cell wall of the wood and is non-leachable in service. To create a commercially-viable process, the modification requires a water-based delivery system, the use of low-toxicity impregnation agents, thermal-curing and no concerns regarding toxicity at end of life of the modified wood product. In previous work it was found that the use of the Maillard reaction appeared to be a promising way of bulking the cell wall (i.e., when reacting lysine, glucose, and citric acid), but with varying success and a high degree of leaching. To reduce leaching and increase of wood bulking, reaction conditions like soaking time, reagent concentrations and reaction temperature were investigated in this work to determine their effect on wood treated with lysine, glucose and citric acid. In general, it was observed that lower soaking times, higher reaction temperatures, and higher reagent concentrations were favourable for the Maillard reaction to proceed.

INTRODUCTION

When exposed to changing atmospheric conditions, wood is susceptible to degradation by fungi and shows dimensional instability. This restricts its use in some situations like outdoor exposure, its use in bathrooms or basements, etc. To prevent degradation, non-durable wood products need to be treated when used in applications where they are susceptible to deterioration.

A possible way to increase the resistance to decay while increasing its dimensional stability, is by controlling the cell wall moisture content of the wood. In order to control the cell wall moisture content, it is necessary that the wood is treated with chemical solutions which diffuse into the wood cell wall and can be fixed in place. The presence of these chemicals will cause bulking of the cell wall, decreasing the cell wall volume accessible to water (Rowell and Banks 1985). The reduction of cell wall moisture content limits the ability of fungal degradative agents to penetrate the cell wall and ensures that most fungal species cannot degrade the wood (Papadopoulos and Hill 2002, Rowell 2006). A requirement of any such wood modification system is that it should be nontoxic under service conditions and, furthermore, there should be no release of any toxic substances during its service life, or after disposal or recycling of the modified wood (Hill 2006). This requires that the polymeric network formed in the cell wall should react with the wood polymers or become entangled with them. Furthermore, the modification polymer should not display hygroscopic behaviour.

A method of impregnation modification that could meet all above mentioned requirements is based on the Maillard reaction. This type of reaction is well-known in food chemistry, where it is responsible for the browning in many foods during baking (Ames 1998; Manzocco et al. 2001). The essence of the reaction is that a reducing sugar, condenses with a compound possessing a free amino group, to give a condensation product (Echavarría et al. 2012). Subsequently, a range of reactions takes place, including cyclizations, dehydrations, retroaldolizations, rearrangements, isomerizations and further condensations, which ultimately lead to the formation of polymers and co-polymers, known as melanoidins (Echavarría et al. 2012). The composition of its chemical structure is relatively unknown due to the complexity of the products that are generated in the reaction (Kim and Lee 2009). The advantage of this reaction is that it is an aqueous process and initiated by heat only, making it relatively straightforward to apply to wood in a commercial process. In addition, the reaction does not require the use of strong acids or bases, which could degrade the wood structure.

In earlier experiments (Peeters et al. 2018), the influence of the Maillard reaction on beech and pine wood was investigated. The wood samples were impregnated with one amine (glucosamine, lysine, or glycine), sugars (glucose or xylose) and an extra reagent to improve the reaction ($MgCl_2$, maleic acid, or citric acid). The samples were soaked for 24 hours in the solutions and reacted at 120°C for 72 hours. The results of the preliminary research showed that when lysine, glucose, or citric acid were reacted a high weight percentage gain (WPG) was obtained (18% for beech and 40% pine). In contrast to most other experiments, a significant amount of the reaction products was still present after leaching. After leaching, the WPG for beech was 11% and 25% for pine. The swelling coefficients showed that swelling occurred only in some of replicates. This preliminary screening reaction has shown that the Maillard reaction does show promise and is worthy of investigation as a potential new wood modification system, however the amount of leaching should decrease tremendously and the increase in volume of the modified wood should be repeatable.

The aim of this research is to investigate the necessary reaction conditions to obtain a lower percentage of leaching and that trap a higher amount of water-insoluble reaction products in the cell wall. For this, different reaction temperatures, soaking times, and reagent concentrations were tested. In general, it would be good if the reactions perform well at low temperatures, since at temperatures under 100°C no special industrial equipment is necessary. The use of short soaking times is also favoured, since then more wood can be treated in a certain period. In previous experiments, chemical reagents were used in concentrations of 0.1 mg mL^{-1}. These concentrations are not economically feasible, so reactions that perform well at lower concentrations are preferable. Lower concentrations could potentially improve the leachability (possibility of less unreacted reagents) and the penetration into the cell wall (lower density of the solution).

EXPERIMENTAL

Small (20 x 20 x 5 mm) and defect-free sapwood specimens (beech – *Fagus sylvatica* L. and pine – *Pinus sylvestris* L.) were used for the modification studies. Samples were cut such that growth rings were parallel to the tangential face, to prevent diamonding during the leaching tests. This size of sample was selected in order to ensure even penetration of reactants into the wood sample and allow for good access of the reagents to the cell wall.

To weigh the wood samples, a balance was used (minimum reading is 0.1 mg). The size of the wood samples was determined with a precision of +/- 0.01 mm with a digital calliper. Air was removed from wood samples during the aqueous impregnation step in a desiccator with a vacuum pump at ambient temperature and 100 mbar. Before determining the volume and weight of the unmodified, modified, and leached wood samples, they were dried for 16 hours at 103°C in an oven. After this the wood samples were removed from the oven and cooled down to ambient temperature in a desiccator over silica gel.

For the reactions lysine (CAS Number: 56-87-1), glucose (CAS Number: 50-99-7), and citric acid (CAS Number 77-92-9) were used. All chemicals were purchased from Sigma Aldrich (Slovenia).

First, the volume and weight of unmodified wood samples were measured. Then, samples were treated in 100 mL aqueous solution combining: 0.1/0.1/0.1, 0.1/0.02/0.02, 0.02/0.1/0.02, 0.02/0.02/0.1 and 0.02/0.02/0.02 g mL^{-1} of lysine/ glucose/ citric acid. These concentrations were chosen to obtain high quantities of reagents that are completely soluble in water, while still having a solution density and viscosity that allows for easy penetration into the wood. Control samples were treated with water only. All experiments were done in 5 replicates. The wood was placed into the amine-sugar solution, then transferred for 1 h into the vacuum chamber to make sure that all the air was removed from the wood lumen. The wood was subsequently soaked for either 8, 24, 48, or 96 hours (four groups) in the solution to allow for diffusion of reagent into the cell wall. The wood samples were then removed from the solution and put into an oven for 72 hours at either 70, 90, 110, or 120°C. To summarise, a total of 11 tests was performed for pine and beech (4 to test the reaction temperature, 4 to test the influence of soaking time and 5 to test the influence of the concentrations). Details can be found in Table 1. After their respective treatment was done, the wood samples were removed from the oven and the volume and weight of the modified wood was determined.

Table 1: Reaction conditions

Changed Parameter	**Reaction T (°C)**	**Soaking time (h)**	**Concentrations lysine/ glucose/ citric acid (mg mL^{-1})**	**Symbols in charts**
Reaction T	70	24	C1: 0.1/0.1/0.1	□
	90	24	C1: 0.1/0.1/0.1	Δ
	110	24	C1:0.1/0.1/0.1	◊
	120	24	C1: 0.1/0.1/0.1	○
Soaking time	120	8	C1: 0.1/0.1/0.1	●
	120	24	C1: 0.1/0.1/0.1	○
	120	48	C1: 0.1/0.1/0.1	◍
	120	96	C1: 0.1/0.1/0.1	⊘
Concentrations	120	96	C1:0.1/0.1/0.1	⊘
	120	96	C2: 0.1/0.02/0.02	⊘
	120	96	C3: 0.02/0.1/0.02	⊘
	120	96	C4: 0.02/0.02/0.1	⊘
	120	96	C5: 0.02/0.02/0.02	⊘

In table 1 can be seen that, when one parameter (temperature, soaking time or concentration) is changed, the two other parameters are held constant. When the temperature and concentration were held constant, values of 120°C and 0.1/0.1/0.1 were chosen, since at that temperature and concentration it was already proven that the Maillard reaction can take place (Peeters et al., 2018). When the soaking time was held constant, the original time chosen was 24 hours as in former experiments, but for the experiments where concentrations were changed, 96 hours were used, since due to unexpected situations, the samples could not be harvested earlier, whereas longer soaking times were not considered critical for the Maillard reaction to occur.

Leaching tests on the wood samples in water were performed in deionised water, which was changed three times a day. 3 leaching cycles of two days each were used until stable weights and sizes were obtained. After each leaching cycle, the wood was dried in the oven and volume and weight gain determined.

The volumetric swelling coefficients (S) were calculated according to the formula (Stamm 1964):

$$S(\%) = ((V_w-V_d)/V_d)x100 \tag{1}$$

where V_w = volume of water saturated wood
V_d = volume of oven dry wood.

The weight percentage gain (WPG) and volume change (VC) were calculated according to the formulas:

$$WPG(\%) = ((W_m-W_u)/W_u)x100 \tag{2}$$

Where W_m= weight of wood after modification or leaching
W_u= weight of unmodified wood

$$VC(\%) =((V_m-V_u)/V_u)x100 \tag{3}$$

Where V_m= volume of wood after modification or leaching
V_u= volume of unmodified wood

RESULTS AND DISCUSSION

This discussion is limited to the post-leaching results as they signify the results of reagents that interacted with the wood or polymerised. WPG and VC were calculated after modification in comparison with the unmodified wood samples. S compares the volume of dry modified, leached wood with the volume of the same specimen in a water saturated state. High values of S indicate a small difference between conditions and a higher degree of swelling. The WPG is an indication for the quantity reagent entered the wood, but the reagents can be present both in the lumen and cell wall. The VC of the wood after modification indicates the amount of final product that has actually penetrated into the cell wall, whereas the swelling coefficient indicates how much space was occupied by the wood modification agents that may have been occupied with water in the absence of modification. An increase in WPG but with relatively low VC and a high swelling coefficient, means that reaction products are present in the cell lumen, but not in the cell wall. On the other hand, with efficient penetration into the wood mass (and not lumina), and good Maillard reaction yield, high VC and low S can be achieved even with a relatively low WPG.

Figure 1 shows that for beech samples after leaching, the VC was not significantly different among the groups of specimens with different modification treatments. A higher WPG is obtained when higher reaction temperatures are used. Soaking time had no influence on the modification yield of beech. Surprisingly, the reaction with lysine as main component was not at all successful. This was unexpected since lysine, being the primary amine, is thought to, together with the sugar, induce the Maillard reaction.

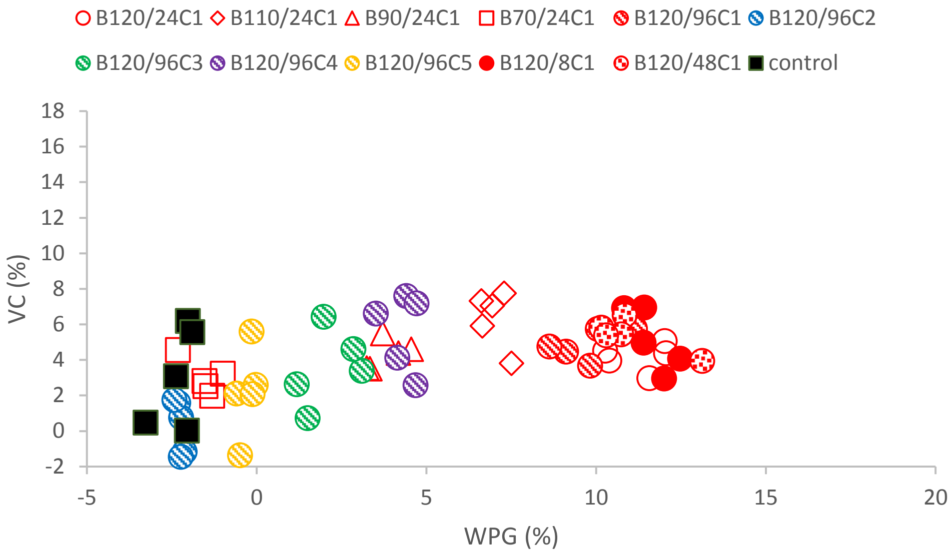

Figure 1: WPG vs. VC of beech (B), which was modified via the Maillard reaction with different values for reaction temperatures, soaking times and reagent concentrations (see Table 1) and subsequently leached.

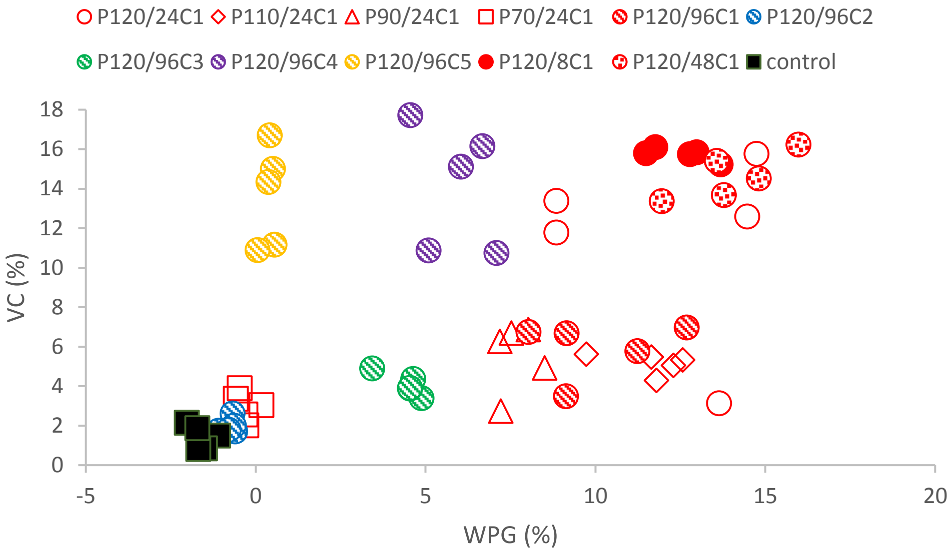

Figure 2: WPG vs. VC of pine (P), which was modified via the Maillard reaction with different values for reaction temperatures, soaking times and reagent concentrations (see Table 1) and subsequently leached.

Figure 2 shows that for pine specimens, a higher WPG was obtained when higher reaction temperatures were used. Interestingly, volume increased and was retained after leaching at a 120°C treatment temperature. Lower soaking times are favoured for pine as a soaking time of 96 hours had a much smaller volume increase at about the same WPG as other treatments with lower soaking times. As with beech, no reaction occurred with an excess of lysine. A volume increase was seen for reagents in low concentrations. This can be explained by the fact that less viscous solutions can penetrate into the wood cell wall more effectively. When citric acid was used in excess, a volume increase was observed, which is expected since citric acid is known to dimensionally stabilize wood (Feng et al. 2014).

In order to be successful, wood modification methods like the one studied here must for polymers in the cell wall. Therefore, samples should show a volume increase compared to the control samples, with concomitant reduction of swelling coefficients. This general trend can be seen with beech treated at 120 °C after being soaked for 96 hours in the solution of 0.02/0.02/0.1 mg mL^{-1} lysine/glucose/citric acid achieving the greatest decrease of S, compared to the control samples (treatment B120/96C4 in Figures 1 and 3). However, in the case of pine, for certain treatments a volume increase is observed, but the swelling coefficients are equal to the control sample (Figures 1 and 4). Yet, the pine treatment P120/96C4 showed the most promising results, since the highest VC and at least a trend towards a reduction in S were recorded.

If the products of the Maillard reaction were to occupy many spaces that the water molecules occupy during swelling of unmodified wood (which would be the optimal outcome of this modification procedure), a much higher reduction in S would have been achieved. From the presented results it is not possible to claim such a success, as the S values of samples with even the highest VC did not differ from the rest of the results. This means that Maillard reaction products do occupy space in the cell wall, but water can still enter the cell walls, creating an additive effect (the cell walls are “bulked” by the Maillard reaction products and the water). Therefore, in future experiments, reagents with less hydrophilic groups should be used to create a less hydrophilic environment.

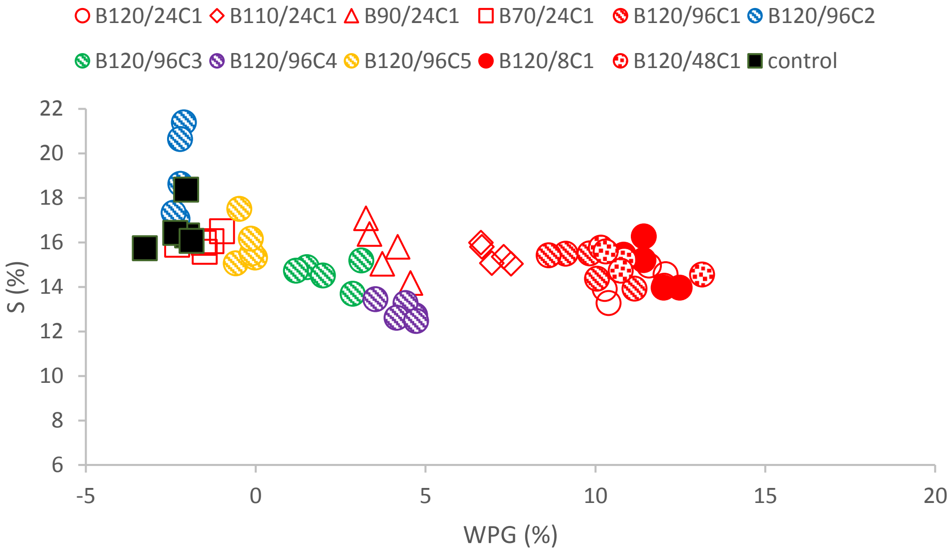

Figure 3: WPG vs. S of beech (B), which was modified via the Maillard reaction with different values for reaction temperatures, soaking times and reagent concentrations (see Table 1) and subsequently leached.

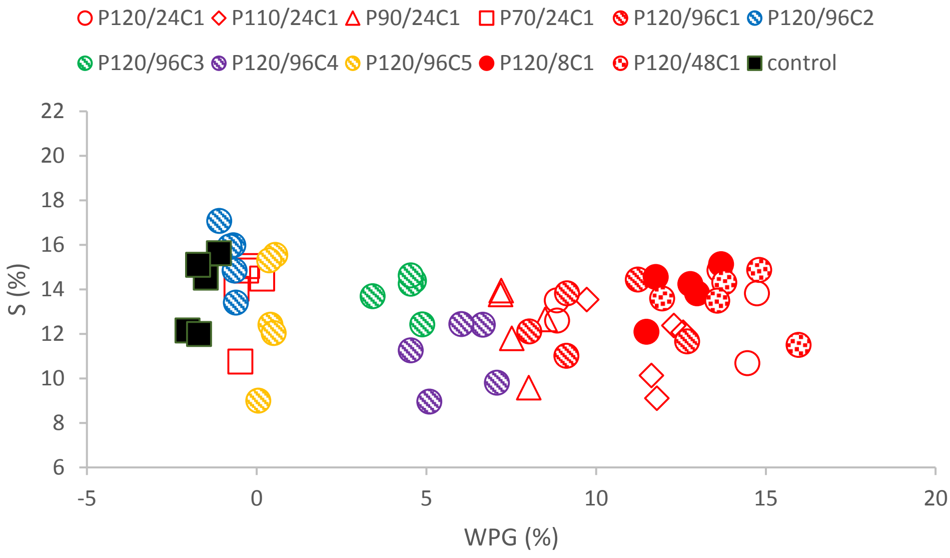

Figure 4: WPG vs. S of pine (P), which was modified via the Maillard reaction with different values for reaction temperatures, soaking times and reagent concentrations (see Table 1) and subsequently leached.

CONCLUSIONS

- From the results it can be seen that the Maillard reaction in wood produces better results at higher reaction temperatures. Therefore, new experiments will be performed at 140 and 160°C. The fact that the reaction doesn't perform well at 70°C and 90°C means that more sophisticated industrial equipment will be necessary if this type of modification will be scaled up.
- Soaking times in reagent solutions as short as 8 hours were enough for a successful Maillard reaction, in samples of the size used in this experiment.
- Concentrations of 0.1 mg mL^{-1} produced the highest WPG. Unfortunately, concentrations of 0.1 mg mL^{-1} are not economical feasible. For pine, however, using lower reagent concentrations of 0.02 mg mL^{-1} or an excess of citric acid resulted in a lower WPG, and there was a high-volume increase, which is favourable.
- Since the experiments where wood was modified with an excess of lysine show no swelling or WPG, the main question is if the Maillard reaction actually took place. It may be possible that an esterification reaction with the free OH groups from the wood constituents and glucose with the carboxylic acid from citric acid is what took place in this case, and the glycine was leached out. To better understand the mechanism of such reactions, future experiments will examine effects decreased lysine concentrations with high concentrations of citric acid and glucose.
- Reagents with fewer hydrophilic reactive groups should be tested in future experiments.

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SESSION SEVEN

Poster Session 2

Wood thermal modification and impregnation: some aspects of double treatment

Bruno Andersons[1], Dace Cirule[2], Ņina Kurnosova[3], Ilze Irbe[4], Ingeborga Andersone[5], Oskars Bikovens[6], Andis Antons[7], Edgars Kuka[8] and Žanete Zommere[9]

[1] Latvian State Institute of Wood Chemistry, LSIWC, 27 Dzerbenes Str., Riga LV-1006, Latvia
[email: bruno.andersons@edi.lv]
[2]LSIWC, 27 Dzerbenes Str., Riga LV-1006, Latvia, [email: xylon@edi.lv]
[3]LSIWC, 27 Dzerbenes Str., Riga LV-1006, Latvia, [email: kurnosova@edi.lv]
[4]LSIWC, 27 Dzerbenes Str., Riga LV-1006, Latvia, [email:ilzeirbe@edi.lv]
[5]LSIWC, 27 Dzerbenes Str., Riga LV-1006, Latvia, [email: i.andersone@edi.lv]
[6]LSIWC, 27 Dzerbenes Str., Riga LV-1006, Latvia, [email: bikovens@edi.lv]
[7]LSIWC, 27 Dzerbenes Str., Riga LV-1006, Latvia, [email:antonsandis@tvnet.lv)]
[8]LSIWC, 27 Dzerbenes Str., Riga LV-1006, Latvia, [email: kukinsons24@gmail.com]
[9]LSIWC, 27 Dzerbenes Str., Riga LV-1006, Latvia, [email:zommerzanete@gmail.com]

Keywords: copper-azole, durability, fixation, impregnation, thermo-hydro treatment

ABSTRACT

The present study deals with results concerning some aspects which are important for improvement of wood durability by applying double treatment that combines thermal modification (TM) and impregnation with biocide. The study was carried out with pine and birch wood by using experimental laboratory impregnation and thermo-hydro modification pilot devices for wood treatment. The examined TM temperature range varied from 150 °C to 180 °C and copper-azole-type biocide solutions of different concentrations were used for impregnation. TM regimes, which ensure high biodurability of wood, reduce wood strength properties by more than 50%, whereas lower treatment intensity enhances wood resistance against rot fungi insufficiently reaching only Class 4 (slightly durable) according to EN 350-1. TM temperatures yielding wood with satisfactory strength properties were selected as the most acceptable for the intended double treatment: 150 °C for birch, and 160 °C for pine. Impregnation showed that the amount of the absorbed solution in wood does not depend on the solution concentration and decreases with increasing wood density. The solution and, consequently, biocide (copper) uptake in TM wood was greater than that in unmodified wood. However, relatively more copper compounds were leached out from TM wood resulting in 20 % less copper fixed in TM wood. The examining of effect of temperature and wet fixation time on copper fixation showed that rising of temperature does not enhance the amount of the fixed copper. To find out the reasons for lower fixation of copper in TM wood, wood chemical composition and non-glucose sugars were analysed by means of wet chemical, FTIR and GC analysis. Degradation of hemicelluloses and decrease of wood pH were recognized as the main wood changes caused by TM at the studied temperature range which affected the strength, durability and biocide fixation.

INTRODUCTION

Currently, industrial wood protection with the second-generation copper-based preservatives does not ensure sufficient durability, especially against copper-resistant and wood staining fungi. Under environmental conditions, copper compounds partly leach out and reduce the fungal resistance of the material. In its turn, the wood thermal modification as an alternative for the improvement of wood durability in the technological regimes, that provide high durability, negatively affects the strength properties. Some attempts to combine thermal modification and impregnation have been made (Wang *et al.* 2013; Baysal *et al.* 2014). Preliminary studies have demonstrated a possibility to achieve improvements in the combined treatment but experiments have been done with small wood samples in laboratory conditions and only some properties of wood have been investigated. Our research comprises a combination of TM and subsequent treatment with copper-organic preservatives and vice versa. The main task is to obtain materials with improved performance, meeting at least the requirements of the durability Class 2 according to EN 350-1, by using milder TM regimes and lower biocide dosage. The study examines TM wood properties with a focus on biocide fixation processes in wood.

EXPERIMENTAL

Studies were carried out on Scots pine (*Pinus sylvestris* L.) and birch (*Betula* spp.) wood. Impregnation was performed with the vacuum-pressure method in a laboratory autoclave (vacuum1 kPa for 30 min, pressure 0.8 MPa for 1 h) and biocide solutions of three concentrations (0.5%, 0.85%, 1.2%) were applied. For TM a WTT (Denmark) pilot device was used and TM at three temperatures with holding time of one hour at the peak temperature were carried out for wood modification of each species: 150, 160, 170 °C – for birch; 160, 170, 180 °C – for pine. TM wood biodurability screening tests with the brown rot fungi strain *Coniophora puteana* BAM Ebw.15 were carried out according to the modified standard CEN/TS 15083-1 (samples dimensions – 20×20×5 mm; the test time - 6 weeks; 6 replicates). Samples leaching was performed according to EN 84. Bending strength was determined according to the standard DIN 52186 (1978). Wood extraction with acetone was carried out in a Soxhlet apparatus for 8 h. Insoluble lignin was determined by the Klason method (TAPPI T222 om-83). Acid-soluble lignin was determined at λ = 205 nm (TAPPI UM-250). Cellulose was determined by the Kirschner's method (Browning, 1967). Sugars were identified by GC (Blakenet *et al.* 1983). The quantitative analysis of copper in wood and solutions was carried out in accordance with DIN 52161-7 (2014) by using atomic absorption spectroscopy (AAS). Cooper fixation in wood was determined after leaching of impregnated specimens according to EN 84.

RESULTS AND DISCUSSION

To select limiting parameters for both double treatment processes, the results concerning effects of the separate treatments on wood performance were evaluated. The TM temperatures for the present study were chosen based on the previous results covering temperature range from 140 to 190 °C. Wood mass loss (ML) due to TM and static bending strength values are presented in Table 1. Pine wood was subject to less degradation than birch wood for which the mass loss was 2-5 times greater at the same TM temperature. With the increase of TM temperature, the decrease of bending strength for pine was close to linear, while for birch major bending strength reduction was caused by increase in temperature from 150 °C to 160 °C. However, only for wood treated at the lowest in the present study applied TM temperatures (150 °C for birch, and 160 °C for pine), the decrease of bending strength was lower than the maximum permitted 40%. Moreover, with increase of the TM temperature, the wood surface hardness decreased (results not presented).

Table 1: Mass loss (ML) and bending strength of thermo-hydro modified birch and pine wood

Birch				Pine			
Treatment tempera-ture [°C]	**Bending strength [MPa]**	**Strength loss [%]**	**ML [%]**	**Treatment tempera-ture [°C]**	**Bending strength [MPa]**	**Strength loss [%]**	**ML [%)]**
unmodified	116.8 (16.4)	-	-	unmodified	93.4 (14.0)	-	-
150	78.7 (18.9)	32.6	0.1	160	61.5 (15.9)	34.2	1.2
160	57.9 (15.5)	50.4	6.6	170	46.2 (20.3)	50.5	6.8
170	51.5 (21.9)	55.9	15.6	180	37.8 (19.6)	59.5	10.6

Standard deviations in parenthesis

One of the benefits gained from wood TM is the improved biodurability against rot fungi. The results of fungi tests with *Coniophora puteana* are listed in Table 2.

Table 2: Mass loss (ML) of thermo-hydro modified birch and pine wood after EN 15038 test and samples leaching according to EN 84

Standards	**EN 15038**			**EN 84**		
Treatment temperature [°C]	**ML [%]**	**DSI**	**ML, controle [%]**	**ML [%]**	**DSI**	**ML, controle [%]**
			Birch			
150	24.1 (6.8)	67.3	35.9 (5.8)	18.0 (4.0)	57.0	31.6 (2.6)
160	6.7 (2.0)	19.9	33.5 (2.7)	20.3 (7.5)	46.8	43.5 (5.7)
170	4.1 (1.3)	10.5	38.8 (3.8)	1.5 (0.7)	3.8	39.6 (4.4)
			Pine			
160	30.7 (8.0)	82.8	37.1 (7.7)	26.0 (7.2)	66.5	39.00 (4.5)
170	12.4 (7.4)	28.0	44.4 (8.7)	17.8 (5.7)	42.6	41.9 (7.6)
180	3.6 (1.1)	6.3	56.8 (4.7)	6.3 (2.8)	14.5	43.8 (9.1)

Standard deviations in parenthesis; DSI – Decay Susceptibility Index

The mass loss (ML) of the pine virulence samples as well as the average moisture content after the test for both the TM and control samples (37% to 80%), indicates favourable conditions for the growth of fungi. All the samples were overgrown with brownish yellow, thick, evenly covered mycelium (except 170 °C TM birch). After leaching, only the highest TM temperatures (170 °C for birch and 180 °C for pine) provided satisfactory wood decay resistance complying to Class 1 (very durable; x≤0.15). TM at lower temperatures provides retention of sufficient wood strength properties. Moreover, despite the insignificant mass losses due to TM and relatively small decrease in wood dry density (by 2-4%), the EMC and linear swelling of TM wood modified at the lowest temperatures decreased in average by ca. 30%. However, the effect of milder TM treatments was small on the wood biodurability improvement. The values of the average ML in fungi tests allow TM birch and pine to classify only as slightly durable which is far from the target – Class 2 (durable).

The changes of TM wood properties are closely related to the treatment effect on the wood component composition (Table 3). Ash content in all samples was similar (around 0.3%). For TM birch and pine modified at lower temperatures, the most essential changes were decrease of the amount of hemicelluloses and increase of acetone extractable compounds, especially for birch wood.

Table 3: The composition of the wood basic components

Treatment temperature [°C]	Extractives [%]	Lignin [%]	Acid soluble lignin (ASL) [%]	Kirschner cellulose [%]	Cellulose [%]*	Hemi-celluloses [%] **
			Birch			
unmodified	2.5 (0.1)	18.8 (0.1)	4.7 (0.2)	50.2	41.3	32.4
150	8.8 (0.2)	17.6 (0.5)	3.7 (0.3)	50.8	44.5	25.2
160	22.7 (0.2)	15.7 (0.1)	2.4 (0.2)	53.3	47.6	11.3
170	17.7 (1.2)	26.1 (0.2)	0.4 (0.1)	55.0	51.8	3.7
			Pine			
unmodified	3.7 (0.4)	26.4 (0.2)	-	54.1	48.4	21.7
160	4.9 (0.2)	28.4 (0.1)	-	56.3	51.7	14.7
170	9.2 (0.3)	34.2 (0.7)	-	56.0	52.1	4.2
180	8.7 (0.3)	40.4 (0.3)	-	53.2	51.5	0

*Cellulose = [Kirschner cellulose – (arabinans+mannans+xylans in the Kirschner's cellulose)]
**Hemicelluloses = [100-(ash+extractives+lignin+ASL+cellulose)]

FTIR-ATR spectra of extractives (not presented in the paper) showed significant quantities of methoxylated phenolic compounds, most probably of lignin origin. In accordance with non-glucose sugars chromatography data (Table 4), birch is characterized by high xylose content (84% of total non-glucose sugars). For pine, mannose composes more than half and xylose approximately one-third of the non-glucose sugars. This sugar ratio is retained also in the TM wood. However, the quantity of non-glucose sugars decreased almost twice for both species modified even at the lowest temperatures. These changes in the TM process confirm their important role in ensuring the wood integrity (i.e., strength) postulated by Fengel (1966). On the other hand, the lower quantity of non-glucose sugars in TM wood reduces degrading intensity of rot fungi and affects the wood/moisture interaction.

Table 4: Composition of non-glycose sugars in unmodified and thermally modified wood

Treatment temperature [°C]	Arabinose [%]	Xylose [%]	Mannose [%]	Galactose [%]	In total [%]
			Birch		
unmodified	0.7 (0.1)	18.5 (1.4)	2.0 (0.5)	1.0 (0.4)	22.1
150	0.3 (0.1)	11.6 (2.0)	0.6 (0.2)	0.1 (0.0)	12.6
160	0.2 (0.1)	6.7 (0.8)	0.7 (0.1)	0	7.6
170	0.2 (0.0)	2.1 (0.2)	0.3 (0.1)	0	2.7
			Pine		
unmodified	1.5 (0.2)	4.9 (0.1)	10.4 (0.4)	1.5 (0.0)	18.3
160	0.2 (0.0)	1.9 (0.2)	6.4 (0.8)	0.6 (0.1)	9.2
170	0.2 (0.0)	1.8 (0.2)	3.8 (0.3)	0	5.8
180	0.1 (0.0)	1.0 (0.1)	1.3 (0.0)	0	2.4

Impregnation of TM wood with water-based preservatives has been little studied (Wang *et al.* 2013; Baysal *et al*. 2014). In the present study of wood double treatment, a copper-azole-type (CA) preservative was chosen for impregnation of TM wood as one of the most widely used for industrial wood protection. The preservative solution concentrations (0.5-0.85-1.2%) were chosen so that only the highest concentration would ensure the toxic value against rot fungi for unmodified wood after leaching.

The biocide solution analysis before and after impregnation showed no changes in copper concentration. The impregnation mode used in the study ensured even penetration of the solution throughout the specimen irrespective of the solution concentration, which was proved by equal wood moisture content through the board cross section. However, higher copper concentration was found near the edges which decreased towards the middle of the board.

The solution uptake and, respectively, the retention of copper in the TM wood, regardless of TM temperature, decreased with the increase of wood density. This testifies that, for TM temperatures under study, the altered wood structure and chemical composition did not affect the total solution/biocide retention in wood. The fixation of biocide ensures wood durability in the service conditions. Copper-organic preservatives fixation has been relatively extensively studied (for example, Freeman and McIntyre 2008; Ye and Morrell 2015; Wang *et al.* 2013). However, the relatively complicated wood preservatives composition and the simultaneously occurring competing reactions in wood have created different opinions regarding fixation. The copper biocide interaction with wood is influenced by various factors: tree species, wood pH, solution composition and concentration, fixation duration and temperature, etc. The copper fixation in unmodified and TM wood, depending on the fixation duration in the wet state and the temperature, was analysed. In Table 5, the results of copper fixation are presented for unmodified and at the lower temperatures modified wood impregnated with a 0.85% solution. The drying mode with the designation “0” means that the specimens were dried at 105 °C immediately after the impregnation. The elevated temperature did not improve but rather reduced copper fixation in both unmodified and TM wood, which can be explained by physical and chemical absorption or adsorption inhibition (Cracium *et al.* 2009).

Table 5. Copper fixation in unmodified and modified wood (CA solution concentration 0.85%)

Drying mode [days/°C]	**Fixation of copper in wood**							
	Birch				**Pine**			
	unmod.	**150 °C**	**unmod.**	**150 °C**	**unmod.**	**160 °C**	**unmod.**	**160 °C**
	[mg/g]		**[% from uptake]**		**[mg/g]**		**[% from uptake]**	
0	0.88	0.62	80.8	48.1	1.07	0.87	76.3	56.3
7/20	0.83	0.77	81.7	55.6	1.09	0.84	75.5	52.2
14/20	0.84	0.73	82.2	52.6	1.03	1.01	75.3	63.5
7/50	0.84	0.52	76.1	41.1	1.05	0.86	75.1	52.5
14/50	0.78	0.62	67.4	44.4	0.99	0.81	73.4	48.6

Compared to unmodified wood, fixation (mg/g) of copper in TM wood was lower by ca. 20%. Retention of copper in the TM wood of both species was about 15% higher, compared with unmodified wood, so, the fixed quantities of copper indicate on a more intensive leaching of copper from the TM wood. This can be caused by TM wood chemical and pH changes. Of greater importance at lower TM temperatures could be cleavage of carboxyl groups, which was confirmed by FTIR spectra (reduction of absorption at 1735 and 1246 cm^{-1}). It is known that pH affects formation of the copper complexes with/when amines and azoles present in the composition (Lee and Copper, 2010). Besides, carboxylic groups (hemicelluloses) play a significant role in bonding cooper in a Cu-ethanolamine treatment (Zang and Kamden 2000; Wang et al. 2013).

CONCLUSIONS

As an alternative to ensure wood durability, the combined thermo-hydro modification (TM)/impregnation treatment was studied. To choose combined treatment parameters, TM of wood in the temperature range of 150-180ºC was carried out. The higher modification temperatures, which ensured wood resistance against rot fungi complying to Class 1 (EN 350-1 classification), reduced the treated wood strength by more than 50%. Therefore, for double treatment research, temperatures reducing wood strength by no more than 40% were chosen, namely, 150°C for birch, and 160°C for pine. As a result of heat treatment, the greater chemical component changes of wood were decrease of hemicelluloses and increase of acetone extractives content. The highest degradation amount was found for xyloses in birch wood and for mannoses in pine wood. For wood impregnation, the CA-type preservative was chosen. As a result of impregnation more of the solution and, consequently, also the copper compounds, were absorbed in TM wood compared to unmodified wood. However, less copper was fixed in TM wood than in unmodified wood. The reasons could be the cleavage of carboxyl groups and the reduction of the wood pH due to thermal treatment.

1. ACKNOWLEDGEMENT

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Hydrophobisation of hardwood surfaces by means of environmentally friendly fine wax particles

Benjamin Arminger[1], Wolfgang Gindl-Altmutter[2] and Christian Hansmann[1]

[1]Wood K plus – Competence Centre for Wood Composites and Wood Chemistry, Konrad-Lorenz-Strasse 24, AT-3430, Tulln [email: b.arminger@kplus-wood.at; c.hansmann@kplus-wood.at]

[2]BOKU University of Natural Resources and Life Sciences, Konrad-Lorenz-Strasse 24, AT-3430, Tulln [email: wolfgang.gindl-altmutter@boku.ac.at]

Keywords: fine particles, hardwood surface, hydrophobation, oil, wax

ABSTRACT

In this paper, aqueous dispersions of fine carnauba wax particles were created and applied on freshly oiled and unoiled wood samples by spraying. Both, walnut (*Juglans regia*) and oak (*Quercus robur*) wood samples showed hydrophobic wetting behaviour when low concentrated particle dispersions were applied on oiled surfaces, resulting in water contact angles of 130° and 123°, respectively. Unoiled samples did not change their hydrophilic behaviour and absorbed water drops during measurements. When highly concentrated dispersions were used, even unoiled surfaces could be turned into hydrophobic, reaching maximum water contact angles above 130°. Nevertheless, standard deviation of contact angles was high and some regions of the samples' surfaces were still hydrophilic. The application of a natural oil layer before spraying could reduce standard deviation and the probability of hydrophilic regions.

INTRODUCTION

Due to excellent mechanical properties combined with attractive appearance, wood is a popular renewable material for both indoor and outdoor applications. Nevertheless, wood processing industry has to deal with several undesired characteristics like swelling and shrinkage, cracking or degradation. Most of such issues show one common denominator: they are results of the wood's interactions with water. Common wood material modification usually aims for improving bulk properties which often is accompanied by weight gain or a change in colour. Many manufacturers and customers of high-priced products made out of special wood species like walnut are interested in maintaining the material's natural character. Therefore, there is a rather new approach of protecting the material by applying a thin but sophisticated surface layer. Since the beginning of this decade, research on hydrophobisation of all kinds of materials is increasing noticeably. Since Prof. Barthlott's extensive work on plant surfaces like the one of the self-cleaning lotus leaf, it is well known that water contact angles higher than 150 ° can be reached when hierarchical structures are created on low surface free energy materials (Barthlott and Neinhuis 1997). Also, different approaches concerning very hydrophobic wood surfaces were published but still, most of the approaches show disadvantages. The surfaces either are based on hazardous (Wang *et al.* 2011) or very expensive chemicals (Gao *et al.* 2016), or application methods are not feasible (Xie *et al.* 2015). Further, nano-structures are generally considered mechanically unstable. Therefore, a focus on durability can be recognized in latest developments (Shah *et al.* 2017).

In this work, thin layers of commercial oil provided by a project partner was applied on wood samples to gain optically and haptically appealing surfaces. Oiled wood surfaces are of hydrophobic nature but usually cannot prevent all wood-water-interactions. Therefore, aqueous suspensions of plant-based fine wax particles were created using a method developed by

Lozhechnikova *et al.* (2017). Particles were filtered and applied on oiled and also unoiled walnut (*Juglans regia*) and oak (*Quercus robur*) wood surfaces to increase surface roughness below the micrometer scale. To increase mechanical stability of the coating, particles were sprayed on the liquid oil before its polymerisation.

EXPERIMENTAL

Materials and particle production

Carnauba wax is the hardest natural wax and has a melting range of 81-86 °C. It was melted in boiling water, dispersed using an Ultra Turrax® device and cooled to form an aqueous particle suspension. Filtration with a 13 µm pore size cellulose filter led to resulting particle sizes of several hundred nanometres. Dispersions of two different carnauba wax particle concentrations were used for spray application on samples. Three-layer panels with oak and walnut wood surface layers were cut into 80 x 60 x 10 mm samples and sanded with abrasive paper of grit designation P320. Wood samples and natural oil were provided by a project partner.

Oil and particle application

A sponge was used to apply a layer of liquid oil on the wood samples. After several minutes of exposure, excess was wiped off using disposable cleaning cloths. Immediately after the oiling, aqueous particle suspensions were sprayed on the liquid oil-wood surface. Water was evaporated in an oven at 60 °C for natural wax dispersions to protect the particles from melting. Spraying-drying-cycles were repeated 12 or 5 times, depending on the dispersion’s particle concentrations. Afterwards, samples were stored in a climate room at 20 °C and 65% relative humidity until oil polymerisation was complete.

RESULTS AND DISCUSSION

Whenever comprehensive protection of wood surfaces is needed, small surface defects can cause problems. Therefore, minimum values of contact angle measurements are of special interest. As this kind of environmentally friendly hydrophobisation is a rather new approach, maximum values are a possibility to show the methods’ potential. Therefore, extreme values of water contact angle (WCA) measurements are pointed out in this section (Figure 1). More detailed results are shown below in Figure 2.

Due to the low amount of particles, low concentrated carnauba wax dispersions were applied in 12 spraying-drying-cycles on oak and walnut wood samples. Figure 1.1 shows images of the maximum and minimum WCA measured on oak and walnut samples. Samples that were oiled just before particle application show maximum WCA higher than 132°.

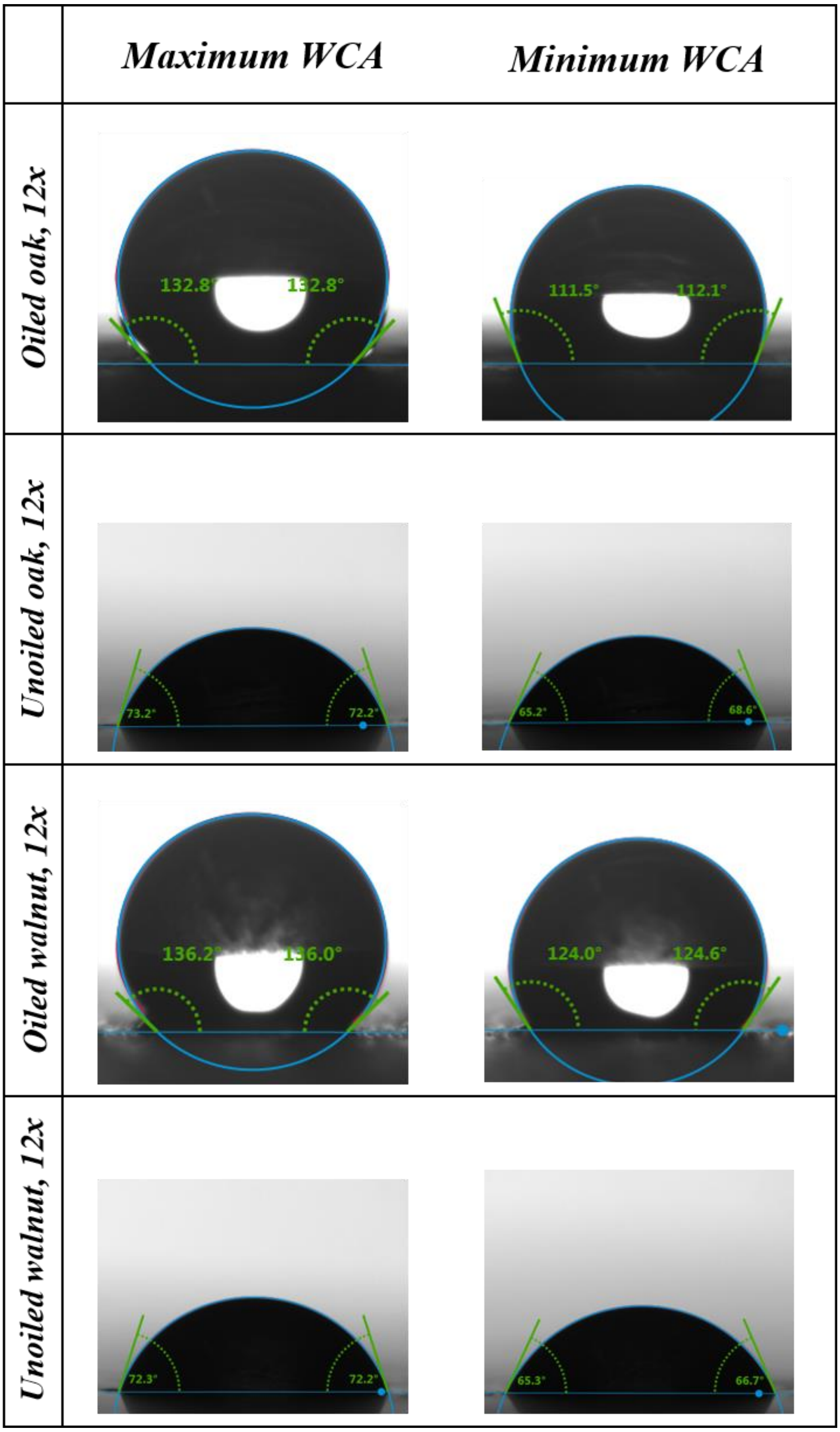

Figure 1.1: Maximum and minimum water contact angles (WCA) of low concentrated carnauba wax particle dispersions sprayed 12 times on oiled and unoiled oak and walnut wood samples.

The standard deviation of WCA measurements on particle-sprayed oak wood was comparatively high. Nevertheless, the minimum WCA measured was 112°, which is an improvement compared to oiled samples without particles, that usually show average values around 100°. The minimum WCA of walnut samples was 124°.

In contrast, unoiled wood samples showed hydrophilic behaviour, which is indicated by WCA smaller than 90° just after drop delivery, and complete water uptake within a few seconds.

Process improvement resulted in higher particle concentrations, which allowed fewer spraying-drying-cycles. Fig. 1.3 shows WCA results of oak samples sprayed 5 times with high concentrated carnauba wax dispersions. Results of oiled samples are similar to the ones sprayed 12 times with lower concentrated dispersions. Unoiled samples now also show hydrophobic behaviour with a maximum WCA value of approximately 131°. Yet, wetting behaviour strongly depends on the dispersion of fine particles, which cannot be controlled sufficiently at the current state of investigation. Therefore, drops deposited on regions with few wax particles still show hydrophilic behaviour.

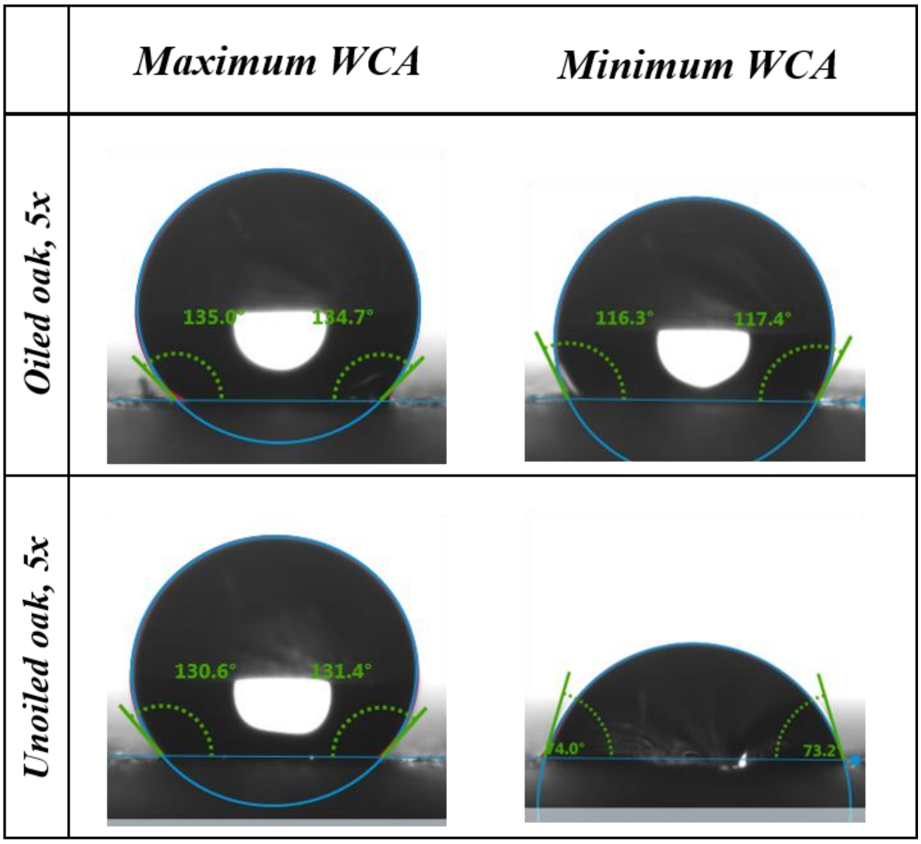

Figure 1.2: Maximum and minimum water contact angles (WCA) of high concentrated carnauba wax particle dispersions sprayed 5 times on oiled and unoiled walnut wood samples.

Figure 2 shows statistical data of the WCA measurements. The dispersion with lower particle concentration led to promising wetting behaviour when sprayed on just-oiled wood surfaces. Walnut wood reached an average WCA of more than 130°, oak approximately 123°. As mentioned before, spraying on unoiled surfaces did not change the wood's natural hydrophilic behaviour. On the other hand, the high concentrated particle dispersion led to similar results on oak wood after only five spraying-drying-cycles with a mean WCA of 125°. Spraying on unoiled oak wood resulted in similar maximum values, but high standard deviation and negative statistical outliers dropped the mean WCA to 116°.

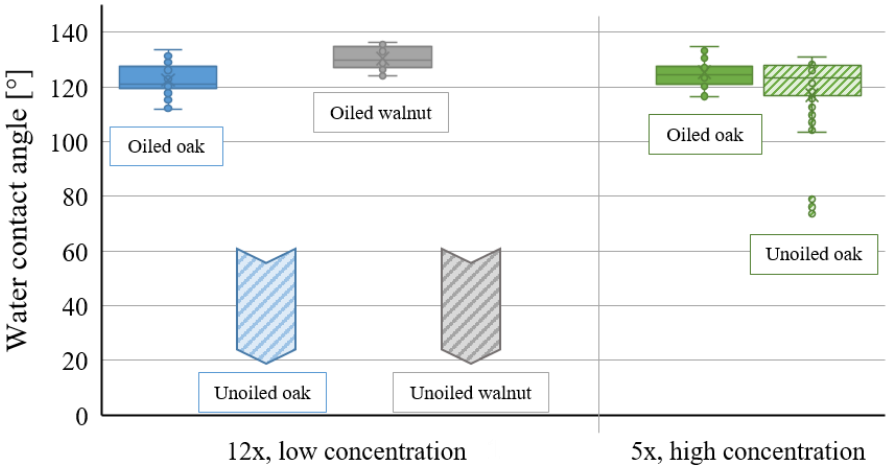

Figure 2: Water contact angle results of oiled or unoiled wood samples sprayed 12 times with low concentration, or 5 times with high concentration dispersions.

CONCLUSIONS

The combination of an oil layer with fine natural wax particles resulted in clearly hydrophobic wetting behaviour, even when an easy to produce, low concentrated particle dispersion was used. Spraying of the same dispersion on unoiled wood did not change the wood's natural hydrophilicity. A more sophisticated natural wax dispersion can even change unoiled wood surfaces into hydrophobic. Nevertheless, the combination with oil reduces standard deviation of water contact angle measurements and the probability of unwanted statistical outliners, which can cause surface defects when in contact with water.

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Further Treatment Option after Longitudinal Wood Compression

Mátyás Báder[1] and Róbert Németh[2]

[1]University of Sopron, Bajcsy-Zs. Street 4, H-9400 Sopron [email: bader.matyas@uni-sopron.hu]
[2]University of Sopron, Bajcsy-Zs. Street 4, H-9400 Sopron [email: nemeth.robert@uni-sopron.hu]

Keywords: longitudinal compression, mechanical properties, memory effect, pleating, steaming, wood bending, wood modification

ABSTRACT

The longitudinal compression is an eco-friendly wood modification treatment, which makes the wood lastingly bendable. Right after the compression process, the compression ratio can be kept for a predetermined time (relaxation). Both increasing compression ratio and increasing relaxation time causes the wood to become more flexible. By the treatment the modulus of elasticity decreases, the deflection at maximum load increases and the needed bending force decreases. Different relaxation times were tested, and it has been proven that after 1 minute of relaxation, the property changes slow down but do not cease. Relaxation time can be up to a daylong and this produces very different properties with at least 6 times higher maximum deflection during 4 point bending tests, compared to the control samples, still without breaking. The treatment produces 3-6 times greater shrinkage in the longitudinal direction during the drying process, depending on the relaxation time. The new properties of the wood can be explained by cell wall deformations.

INTRODUCTION

The longitudinal compression of wood is a combined thermo-hydro-mechanical treatment, also known as pleating (Báder and Németh 2018). By longitudinal compression the bending modulus of elasticity (*MoE*) and the required bending force decrease dramatically and provide great flexibility to the wood (Báder and Németh 2017, Kuzsella 2011). These property changes of the wood can be explained by cell wall deformations (Kollmann 1951, Sandberg and Navi 2007). The wood will bend more easily and in smaller radii compared to steam bending, even when it is cold. Thus, there can be found some innovative, high added value of the bent wood. The products are mostly used in furniture industry for example as chairs and skirting, furniture rim, mattress coil springs. It can be also used in interior design as wooden handrails, coat hooks, applied arts, etc. (Báder 2015). Other applications are also possible, e.g. vibration dampening tool shafts, car panels, wood toys, medical aids, etc. (Báder 2015). In areas where corners have to be avoided, it can be an excellent raw material for product design, for example, ship and aircraft furniture (Vorreiter 1949, Báder 2015).

The procedure (like the Thonet-method) requires high quality hardwood material. Before compression, the wood has to be plasticized by steaming (Ivánovics 2006, Sandberg and Navi 2007). The sample is usually compressed by 20% compared to its original length. Following the method, the specimen is wet at the beginning, and as long as the moisture content is high, it can be bent more easily (Báder and Németh 2017). The compressed materials are ready to use immediately after the treatment, but they can be also stored, preferably in foil at cold temperatures.

EXPERIMENTAL

The raw material was Sessile Oak (*Quercus petraea* (Matt.) Liebl.), from the Sopron region, Hungary. The dimensions of the samples were 20×20×200 mm (Radial × Tangential × Longitudinal). We used steaming at atmospheric pressure in saturated atmosphere. After steaming, the samples were longitudinally compressed, while the temperature was kept at 90 °C to 100 °C degrees. Longitudinal compression can be achieved as the workpiece is kept straight during the compression process, through supports on the sides. The device is developed to operate in an Instron 4208 (Instron Corporation, USA) universal material testing machine. All samples were compressed by 20% compared to their original lengths, at a rate of 30 $mm \cdot min^{-1}$. After compression, the 20% compression ratio was kept for a predetermined time, allowing the wood to undergo viscoelastic relaxation. During relaxation, the force required to keep the sample in compressed state decreased (Báder and Németh 2018). All relaxations were made in the laboratory compression chamber (Table 1).

Table 1: Test methods and labelling of oak samples.

Marking	Pieces	Sample marking explanation
OC	20	Control
OSC	20	Steamed Control
O0m	20	Compressed without relaxation
O1m	20	Compressed with 1 minute of relaxation
OLm	3	Compressed with a long-time relaxation (averagely 900 minutes)

At the OLm samples the heating was switched off during the relaxation. In this case, the compression device cooled down with the sample, and thus the moisture loss was eliminated. After treatment, the samples were dried at a temperature of 40 °C for 48 hours, then conditioned at 20°C and 65% relative humidity (*RH*) until a constant weight was reached.

Based on the method described by Báder and Németh (2017), the height of the samples (*h*) was 12.5 mm, and the width (*b*) was left the original size. An Instron 4208 material testing machine was used for 4 point bending tests. The loading rate was 20 mm/min, except for control samples (8 mm/min), according to the Hungarian standard MSZ 6786-5 (2004). Tests were stopped when the load dropped with no recovery. The determination of the *MoE* comes from the work of Báder and Németh (2017), using the loading span displacement (Δw) corresponding to the difference between the 10% and the 25% of the maximum load (ΔF) (Eqn. 1).

$$MoE=(\Delta F \cdot a^2 \cdot (3 \cdot L-4 \cdot a))/(b \cdot h^3 \cdot \Delta w) \qquad (1)$$

where a is the distance between the loading span and the nearest support span (50 mm), and L is the distance of the support spans. The maximum deflection of the sample (y_{max}) came from Eqn. 2, based on Báder and Németh (2017).

$$y_{max}=1.1563 \cdot (w \cdot (3 \cdot L^2-4 \cdot a^2))/(4 \cdot a \cdot (3 \cdot L-4 \cdot a))-0.7345 \qquad (2)$$

where w is the highest displacement of the loading span till the fracture of the sample. Eqn. 2 is applicable for materials with high bendability.

RESULTS AND DISCUSSION

Mechanical changes

The *MoE* for the control samples averaged 10.0 GPa and the stress change at 5 mm load span displacement for the control samples averaged 100.0 MPa. The results of the longitudinal compression and short-time relaxation are shown in Figure 1.

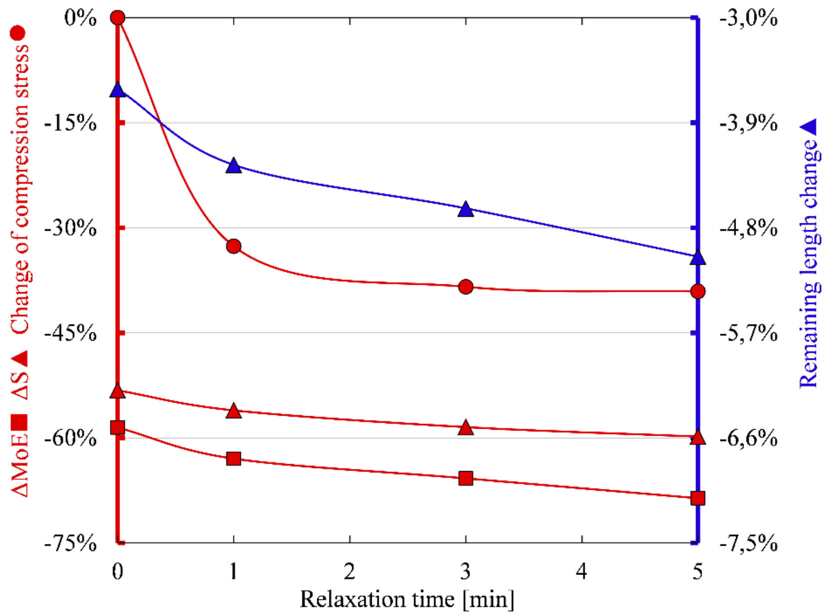

Figure 1: Change of the mechanical and physical properties after compression with the increasing relaxation time. Abbreviations: ΔMoE - change of Modulus of Elasticity; ΔS. - Stress change at 5 mm load span displacement.

The differences between the mechanical properties of control and steamed control samples are negligible so it is not necessary to discuss them separately. The stress at 5 mm load span displacement shows us the first advantage of the pleating method. It decreased to half or less by the treatment (Figure 1). The longitudinal compression resulted in a decrease of *MoE* with 59.0%. While the deflection of control samples averaged 9.3 mm till the break, both compressed and short-time relaxed samples had at least 3 times higher deflection (Figure 2a), and almost the same force needed for the bending process. Furthermore, with a large increase of relaxation time (*OLm* samples) the deflection ability increased so much that the samples did not break during the bending tests. The high deflections mean high bendability, which is the most important property for utilization of this material (Figure 2a). For *OLm* samples the maximum deflection is at least 6 times higher than in case of control samples.

The point of the maximum force and the break move away from each other with the increasing relaxation time. This indicates an increasing ductility due to increased relaxation time. The deformability has a strong inverse correlation with *MoE* (Ashby and Jones 2003). Figure 2b represents the change of the *MoE*. The slope at the beginning of each graph decreases with the increased relaxation time. At the greatest force peaky graphs can be observed on Figure 2b for the control samples. These peaks gradually become rounded both by compression and increasing relaxation time. Finally, *OLm* samples can undergo significant plastic deformation before fracturing: they show ductile properties (Hayden et al. 1965), as also represented in Figure 2c. All these changed properties led to a new material with the major advantage of easy bendability.

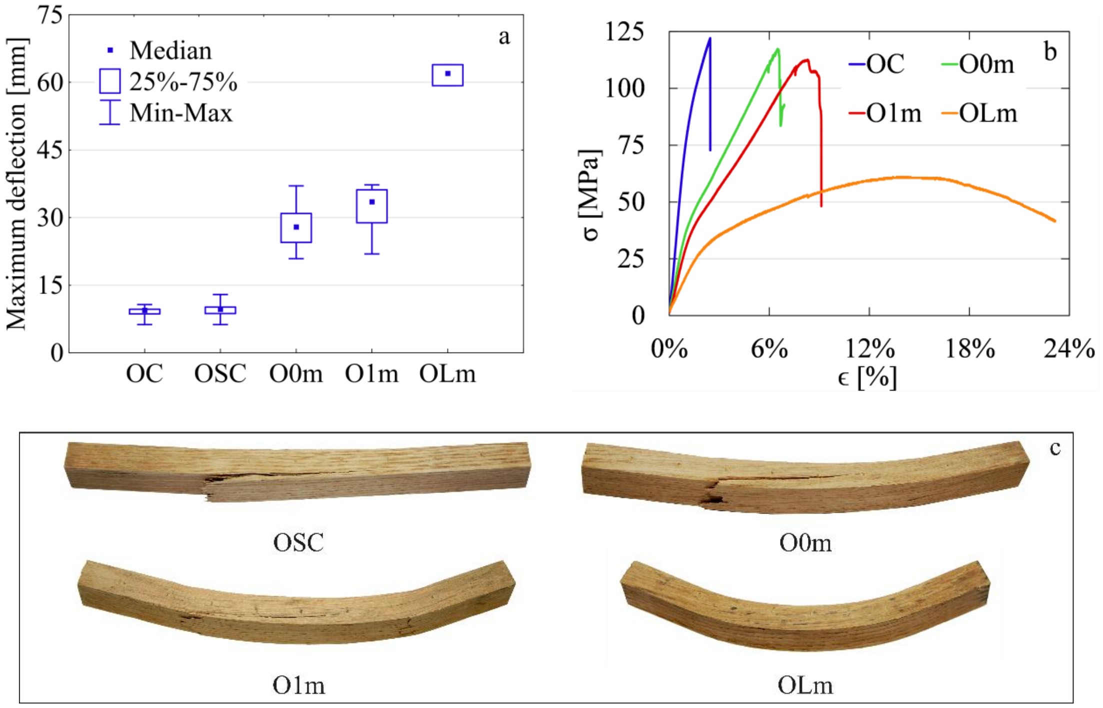

Figure 2: The maximum deflections during 4 point bending test (a), typical Relative deformation – Bending stress graphs for the different treatments (b) and images of crack patterns for different modification methods (c). Abbreviations: OC-control sample; OSC-steamed control sample; O0m, O1m - longitudinally compressed samples with 0 and 1 minute of relaxation time; OLm - compressed and long-time relaxed sample.

Physical changes

The remaining shortening after pleating represents the resistance of wood against the compression, and the remaining shortening is proportional with the force needed to bend the wood (Segesdy 2003). The length change after drying to 0% moisture content was calculated from the difference of length changes under wet and normal conditions. After longitudinal compression, shrinkage is 3 times higher during the drying (Figure 3a). The relaxation process increases the shrinkage too, from 0.51% to 0.68% in the first minute. With the long-time relaxed samples, the shortening amounts to 0.94% during drying. Compared to control samples, this means about 6 times higher shrinkage. The explanation of this phenomenon can be due to the curved cell walls, because this way a part of the far greater transverse shrinkage is added to the longitudinal shrinkage. This is also evidenced by the remaining length change after the treatment (Figure 3b).

Optimal relaxation time

Analyzing the change of compression stress during relaxation, in the first 2 seconds, the compression stress falls by 12.1%. In the next 2 seconds, the compression stress falls by 4.7%, then only by 3.1% and by 2.4%, and so on, compared to the starting value. After 1 minute relaxation time, the changes slow down considerably. If we are looking for the optimal relaxation time based on the mechanical changes, 1 minute relaxation is suggested. After 1 minute relaxation time, the maximum deflection increases to 110% compared to the compressed wood without relaxation, and to 353% compared to the control samples, in accordance with the decrease of *MoE* (89.3% and 37.0%, respectively). Bending stress at 5 mm load span displacement decrease to 43.9% by longitudinal compression and 1 minute relaxation time, compared to the control samples (Figure 1). Of course, to meet individual demands, longer relaxation times can be chosen. A higher compression ratio (Buchter et al. 1993) or a long-time relaxation is needed to further enhance the deflection, but this results in a very slow process both for industrial and laboratorial production. However, maximum deflection increases a lot, just as shrinkage increases during the drying process.

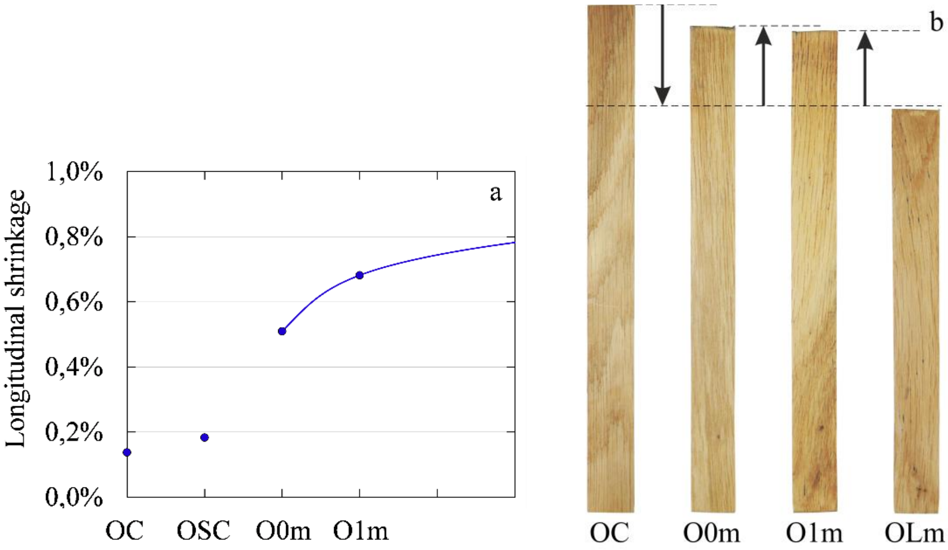

Figure 3: Length change during the drying process, depending on the relaxation time (a) and remaining shortening of the samples after different treatments (b). Abbreviations: OC - control sample; OSC - steamed control sample; O0m, O1m - longitudinally compressed samples with 0 and 1 minutes of relaxation time.

CONCLUSIONS

This study was performed to determine some mechanical properties such as *MoE* and some physical properties such as deflection of the longitudinally compressed Sessile Oak, produced with different relaxation times.

Higher compression stress reduction during relaxation means greater remaining shortening of the material, and these are indicators of higher deflection ability and higher relative deformation, and lower *MoE*. Furthermore, pleating produces 3-6 times greater shrinkage in the longitudinal direction during the drying process, depending on relaxation time.

Different relaxation times were tested, and it has been proven that after 1 minute relaxation time, the change of the material properties slows down extremely, so the generally recommended relaxation time is 1 minute as an ideal combination of economic relaxation time and increasing of bendability. This results in an increase in maximum deflection during 4 point bending tests to 353%, and in a decrease to 37% in *MoE* and to 44% in bending stress at 5 mm load span displacement, compared to the control samples. To meet special requirements for the product, both the compression ratio and the relaxation time can be changed. A long relaxation time results in a wood material with plastic properties with a 6 times higher deflection compared to the compressed samples without relaxation, still without breaking, but this slows down the production and increases its costs.

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Effect of combined modification processes on the physical properties of wood

Miklós Bak[1], Róbert Németh[2], Norbert Kelemen[3]

[1]University of Sopron, Bajcsy-Zsilinszky u. 4, H-9400 Sopron, Hungary [bak.miklos@uni-sopron.hu]
[2] University of Sopron, Bajcsy-Zsilinszky u. 4, H-9400 Sopron, Hungary [nemeth.robert@uni-sopron.hu]
[3] University of Sopron, Bajcsy-Zsilinszky u. 4, H-9400 Sopron, Hungary [kelemenn15@student.uni-sopron.hu]

Keywords: combined modification, heat treatment, impregnation, paraffin wax, physical properties

ABSTRACT

The investigated treatment in this study was a heat treatment in paraffin wax at 180°C or 200°C with 5 hours duration. Impregnation was accomplished by the cooling of the material in the paraffin after heat treatment step, from the treatment temperature to 100°C. During this cooling step, wood material was saturated by the melted paraffin wax. After taking the samples from the hot paraffin, wax was hardened in the cell lumen. In addition, samples were heat treated without impregnation (normal heat treatment) to determine the effect of additional impregnations to the effect of heat treatment. Samples of beech wood were used for the tests. Mass loss, colour change, swelling, bending strength and compression strength was investigated. Colour changed remarkably in case of both heat treatment and combined treatment. However, colour change as a result of the combined treatment was larger. Slight increase of red- and yellow hue, and large decrease of the lightness was observed in case of normal treatment. Contrarily, in case of combined treatments, red hue decreased slightly, while a significant decrease of yellow hue was observed. Mass loss was slightly higher in case of combined treatment, which result can be explained by the different heating medium. Heat transfer is more intensive in case of the paraffin wax treatment medium. Interesting result was found, that paraffin uptake was higher in case of treatment at 180°C compared to the treatment at 200°C. Bending strength decreased by 25-40% depending on the treatment. Compression strength increased by 30% as a result of normal heat treatment, while it remained unchanged in case of the combined treatment. Swelling properties were decreased as a result of heat treatment, but in case of the combined treatment swelling was remarkably lower compared to the simple heat treatment.

INTRODUCTION

The thermal treatment of wood was a research topic long ago, and the processes were permanently optimized in different countries. The first trials by Tiemann (1920) showed already, that high temperature drying increases the dimensional stability. But targeted investigations only began later (Stamm and Hansen 1937). During time, different processes have been widely used in Europe (Sandberg *et al.* 2017). The advantage of paraffin wax is its water repellent and nontoxic nature.

Waxes are natural or synthetic substances depending on their origin. Waxes are used for wood surface finishing and coating from the ancient times. Since biocides, due to EU regulations are increasingly restricted, waxes and wax emulsions are becoming one of the most important solutions for non-biocidal wood protection in outdoor applications to improve durability, dimensional stability and sorption properties. Furthermore, treatments with waxes slow the photodegradation process of wood as well (Lesar *et al.* 2011). With the impregnation method, the cell lumens can be filled with wax. An advantage of wax impregnation of wood is the improvement in wood's mechanical properties. For example, the hardness can be increased in beech wood up to 86 to 189% in the longitudinal and lateral directions, respectively. Other mechanical properties of wood, like compression, bending or impact-bending strength can be also improve as the effect of impregnation with different waxes (Scholz *et al.* 2010). Both the heat treatment and the impregnation with waxes provide some dimensional stability for wood, but only limited. The mode of action of these treatments is different. In case of heat treatment the effect is mainly the removal of hydroxyl groups through the thermal degradation of the cell wall polymers. In case of impregnation, the effect is the clogging of the cell lumens and cell wall pores by waxes, thus the occlusion of water from the cell wall. With the combination of these treatments, it is possible to improve the dimensional stability of wood, as the effects of different mode of actions are added.

EXPERIMENTAL

Modification processes

Beech (*Fagus sylvatica*) wood was heat-treated in paraffin wax. The dimensions of the treated samples (laths) were 30×50×320 mm^3 (TxRxL). Macrocrystalline paraffin wax was used as heat treatment medium. The paraffin bath ensured the deficiency of oxygen during the treatment as the samples were immersed in the paraffin. The investigated treatment was a heat treatment in paraffin wax (combined treatment) at 180°C or 200°C with 5 hours duration. Impregnation was accomplished by the cooling of the material in the paraffin after heat treatment step, from the treatment temperature to 100°C. During this cooling step, wood material was saturated by the melted paraffin wax. After taking the samples from the hot paraffin, wax was hardened in the cell lumen. Six samples (laths) with an initial moisture content of 12% were used for each schedule. The samples were placed directly in the warm paraffin bath having temperature of 80°C without preheating. At the end of the process the samples were removed from the paraffin bath at 100°C, to avoid hardening of the wax before the removal of the samples. Samples were stored after treatment under standard conditions (T=20°C, φ=65%). Untreated and air-dried laths having the same dimensions served as the control. To be able to show the additional effect of paraffin impregnation to the heat treatment, samples with the same dimensions and parameters were heat treated (HT) together in the chamber with the paraffin treated samples. The heat treatment medium in this case was atmospheric air. Thus, all samples (both HT and combined treatment) were heat treated under the same conditions at the same time, excepting treatment medium. Untreated samples were used as control. Samples of beech (*Fagus sylvatica*) were used for the tests.

Colour measurement

Colour analysis was carried out according to the CIELab colour system. The moisture content of air-dried, conditioned (T=20°C; φ=65%) samples was measured. For colour measurements, a Konica-Minolta CM – 2600d model spectrophotometer was used. Colour of the initial laths was measured before and after the heat treatment at five points on each lath.

Mechanical properties

Bending strength (MOR) and compression strength parallel to the grain was determined on normal heat treated and heat treated/impregnated samples. Untreated samples served as control. To determine the MOR, a standard three-point bending method was used, based on the standard MSZ 6786-5/1984. To determine the bending strength, a method based on the standard MSZ 6786-8/1984 was used. 20 samples were tested for both treated and untreated material.

Swelling

To determine swelling, 20×20×30 mm (radial × tangential × longitudinal) samples were cut from the heat-treated laths; there were 20 pieces from all treatment types investigated. 20 pieces of untreated samples served as the control. The samples were dried at 105°C until a constant mass and then the dimensions were measured in the radial, tangential and longitudinal directions. Thereafter, the samples were stored under water for 7 days and finally the dimensions were measured again.

Swelling was determined according to Eq. (1):

$$S_{r,t} = \frac{l_u - l_0}{l_0} \cdot 100 \ (\%) \qquad (1)$$

Where, $S_{r,t}$: swelling, radial, tangential or longitudinal (%)
l_u : dimension after wetting (mm)
l_0 : dimension in dry state (mm)

RESULTS AND DISCUSSION

Mass loss was significantly higher in case of combined treatment, which result can be explained by the different heating medium. Heat transfer is more intensive in case of the paraffin wax treatment medium. Interesting result was found, that paraffin uptake was higher in case of treatment at 180°C (278,37 kg/m^3) compared to the treatment at 200°C (144,29 kg/m^3), however, treatment duration was the same in both cases (Table 1).

Table 1: Mass loss and paraffin uptake as a result of different modification methods

Treatment	**Mass loss (%)**	**Paraffin uptake (kg/m^3)**
Combined 180°C	4,91 %	278,37
Combined 200°C	12,10 %	144,29
HT 180°C	2,41 %	-
HT 200°C	4,11 %	-

Colour changed remarkably in case of both heat treatment and combined treatment, but colour change as a result of the combined treatment was larger. However, there was a difference between normal and combined treatments (Figure 1). Slight increase of red- and yellow hue, and large decrease of the lightness was observed in case of normal treatment. Contrarily, in case of combined treatments, red hue decreased slightly, while a significant decrease of yellow hue was observed. Additionally, the decrease of lightness was more intensive compared to the normal treatment. The reason for the different colour change as a result of the two investigated treatment types treatments is the different treatment medium. The liquid treatment medium ensured a more intensive heat transfer that led to more intensive colour change. Additionally, the paraffin became dark coloured as a result of the treatment as well. This can be explained by the precipitation of the heat degradation products from wood material. The presence of this discoloured paraffin led to a darker colour of the material after heat treatment as well.

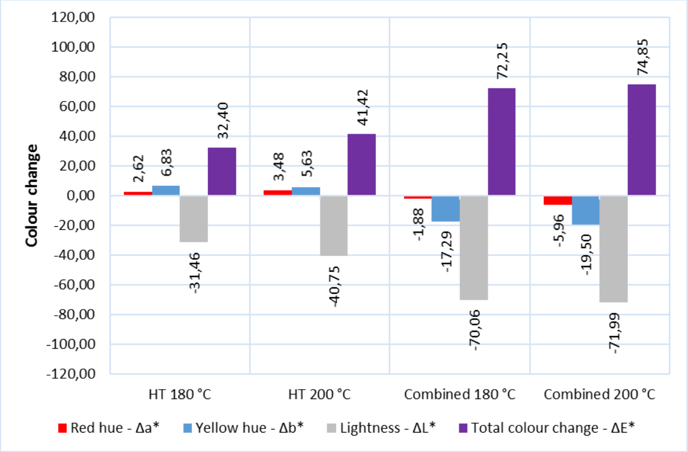

Figure 1: Change of colour properties as a result of different modification methods

Bending strength decreased in case of all investigated treatments significantly, compared to the control (Figure 2). Bending strength decreased by 25-40% depending on the treatment type. Comparing the results of normal and combined treatments at identical treatment temperatures, there was no significant difference between them. These results indicate an intensive heat degradation of the cell wall structure. However, our hypothesis was that the presence of solid paraffin in cell lumens will result in higher bending strength compared to the normal heat treated material, this was not supported by our results. The explanation for this might be in this case as well, that the more intensive heat transfer in the paraffin medium resulted in somewhat higher heat degradation that compensated the strengthening effect of the presence of paraffin in the cell lumens of wood.

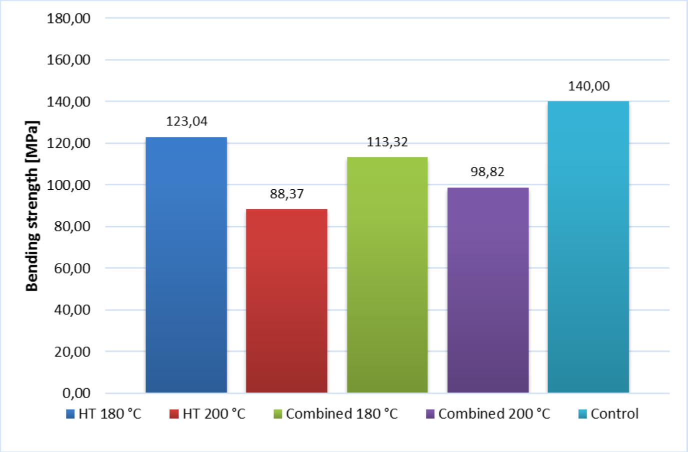

Figure 2: Change of bending strength as a result of different modification methods

Compression strength increased in case of normal treatments significantly, compared to the control, while in case of combined treatment, there was no significant difference (Figure 3). Compression strength increased by 30% as a result of heat treatment, while it remained unchanged in case of the combined treatment. Higher treatment temperatures resulted in slightly lower compression strength values. These results support again the theory, that the heat degradation of the cell wall components is increased when using a liquid (paraffin) as heat treatment medium, because of the more intensive heat transfer. The result of this phenomena is the lower mechanical properties in case of wood material heat treated in paraffin. This result is even more interesting, if we take into account that bending strength is more depending on the properties of cellulose and hemicelluloses (tensile properties), while compression strength is more dependent on the condition of lignin. The lower compression strength values of combined treatments compared to the normal heat treated material indicates a higher degradation of lignin, using a more intensive heat transfer during the heat treatment.

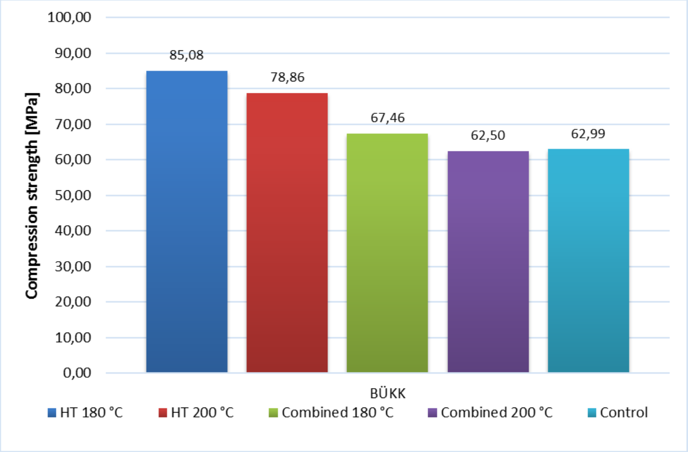

Figure 3: Change of compression strength as a result of different modification methods

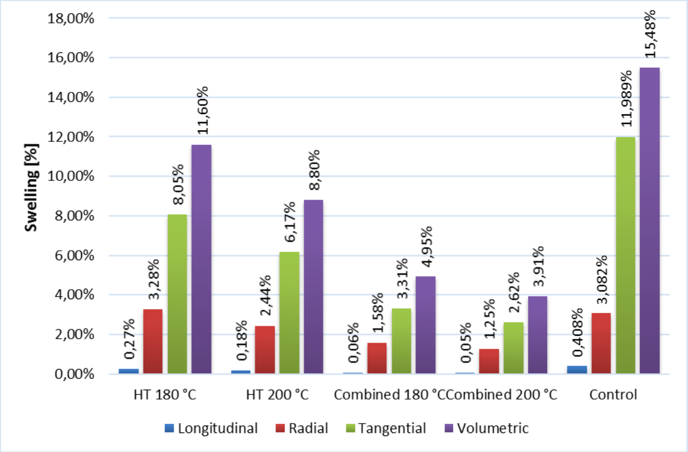

Figure 4: Swelling properties of beech wood before (control) after normal (HT) and combined heat treatments

Swelling properties were decreased as a result of all investigated treatments, but in case of the combined treatment swelling was remarkably lower compared to the normal heat treatment (Figure 4.). Dimensional stability increased in proportion with the treatment temperature, as higher treatment temperature resulted in lower swelling values in case of both combined and normal treatments. Promising result was found that combined treatments resulted in much lower swelling compared to the normal treatments. This can be explained from one hand again with the higher heat degradation because of more intensive heat transfer, resulting in higher efficiency against moisture uptake. From the other hand, this result can be explained by the occlusion of the cell lumens and the water repellent effect of paraffin wax.

CONCLUSIONS

The goal of this study was to investigate the effect of a combined wood modification process, consisting of a heat treatment step in paraffin wax, followed by an impregnation step with the paraffin by the cooling of the samples in the paraffin. Results showed significant differences compared to a normal heat treatment process regarding the mass loss, colour, mechanical and swelling properties as well. Mass loss and darkening of the material increased as a result of combined treatment compared to the normal process. No significant difference could be found in case of bending strength between the effect of different treatment processes, while there was a decrease in case of combined process when using a combined treatment. These results are explained by the more intensive heat transfer in case of a combined treatment compared to a normal process. However, dimensional stability increased remarkably in case of combined treatment, because of the favourable effect of paraffin impregnation additionally to the effect of heat treatment.

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Bending properties and strain fields around knots in thermally modified timber

Joran van Blokland[1], Stergios Adamopoulos[2], Anders Olsson[3] and Jan Oscarsson[4]

[1]Department of Forestry and Wood Technology, Linnaeus University, 351 95 Växjö [email: joran.vanblokland@lnu.se)]
[2]Department of Forestry and Wood Technology, Linnaeus University, 351 95 Växjö [email: stergios.adamopoulos@lnu.se)]
[3]Department of Building Technology, Linnaeus University, 351 95 Växjö [email: anders.olsson@lnu.se)]
[4]Department of Building Technology, Linnaeus University, 351 95 Växjö [email: jan.oscarsson@lnu.se)]

Keywords: four-point bending, modulus of elasticity, Norway spruce, strain measurement, strength prediction, ThermoWood®

ABSTRACT

Thirty-two (32) boards of Norway spruce with cross-sectional dimensions of 145×45 mm^2 were first tested non-destructively in a four-point static bending test, were then thermally modified according to the ThermoWood® process, and were finally tested destructively in the mentioned test set up. For one of these boards, the 2D strain fields occurring due to pure bending were recorded, both before and after thermal modification, over the surface of a knotty part of the board using a non-contact optical deformation measurement system. The objectives were to get more insight into the static bending behaviour of thermally modified timber (TMT), specifically with regard to the local and global modulus of elasticity (MOE) and their respective relationship to bending strength, and the strain development around a cluster of knots. The bending strength was significantly reduced by thermal treatment, whereas the effect on the MOEs was limited. Linear regression analyses demonstrated that bending strength of TMT can be predicted by employing stiffness as indicating property. Strain field measurements showed that at the examined levels of loading the quantity and distribution of strains in a knotty area were not influenced by thermal modification. It was therefore suggested that the influence of thermal modification on global stiffness, as well as on local stiffness around knots, is limited.

INTRODUCTION

Thermal modification is an environmental friendly technology that is used to improve certain material properties of wood (Militz and Altgen 2014). Thermally modified wood products are typically applied as outdoor cladding or decking material where wood with a high shape-stability and durability is required. Yet, at present, thermally modified wood is not allowed for use in structural applications, because of the loss in mechanical strength and ductility that can both be attributed to the modification process (Bengtsson *et al.* 2002, Widmann *et al*. 2012). On the other hand, previous results on the bending behaviour of thermally modified timber (TMT) indicate that TMT has a potential for use in structural applications, mainly when stiffness is the governing design parameter (Bengtsson *et al.* 2002). In this paper, the static bending properties of TMT were evaluated by (1) investigating the local- and global modulus of elasticity (MOE) and their relationship to bending strength (f_m), and (2) by an analysis of strain fields around knots on a board's surface. The purpose of this paper is to provide a better understanding of the static bending properties of TMT since such knowledge will be useful for exploring the potential of predictions of these properties. For example, the development of finite element models analysing the mechanical behaviour of TMT around areas where high stresses occur might further improve bending stiffness and strength predictions.

MATERIALS AND METHODS

In total, 32 boards of Norway spruce (*Picea abies* L. Karst) with cross-sectional dimensions of 45×145 mm^2 and 3.6 to 4.8 m in length were used. The boards were sawn with a 2X-log pattern from 32 logs harvested in central Sweden (*i.e.* one board from each log). The mirror 32 boards were used as controls (Figure 1), but these boards were not further evaluated in the research presented in this paper. The sawing was carried out at Stora Enso's sawmill in Gruvön, Sweden.

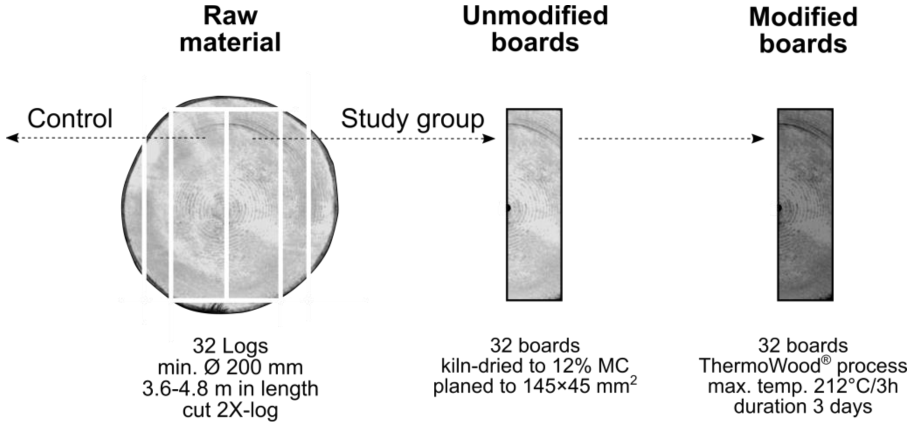

Figure 1: Preparations of boards

First, the 32 unmodified boards were tested non-destructively in a four-point static bending test following European standard EN 408 (2010). An overview of the test set up using the universal testing machine ALWETRON TCT 100 (Lorentzen & Wettre AB, Stockholm, Sweden) is shown in Figure 2. The mass and volume of each board were determined to calculate the density (ρ) [kgm^{-3}]. The moisture content (MC) [%] of all unmodified boards was obtained by using a pin-style moisture meter (RDM-2S, Delmhorst Instrument Co., Towaco, USA). Global ($E_{m,g}$) and local ($E_{m,l}$) moduli of elasticity were calculated according Eqns. 1 and 2, respectively:

$$E_{m,g}\ [\mathrm{MPa}] = \frac{L^3(F_2-F_1)}{th^3(w_2-w_1)}\left[\frac{3a}{4L}-\left(\frac{a}{L}\right)^3\right] \quad (1)$$

$$E_{m,l}\ [\mathrm{MPa}] = \frac{3al^2(F_2-F_1)}{4th^3(v_2-v_1)} \quad (2)$$

in which h is the height [mm] and t the thickness [mm] of the board at mid-span, and a is the distance from the support to the load-point [mm]. In Eqn. 1, L is the span over which global deflection was measured [mm], F_2-F_1 is the load increment [N] and w_2-w_1 is the corresponding increment in global deflection [mm], both taken from a straight part of the F-w curve. In Eqn. 2, l is the span over which the local deflection was measured [mm], F_2-F_1 is the load increment [N] and v_2-v_1 is the corresponding increment in local deflection [mm], both taken from a straight part of the F-v curve.

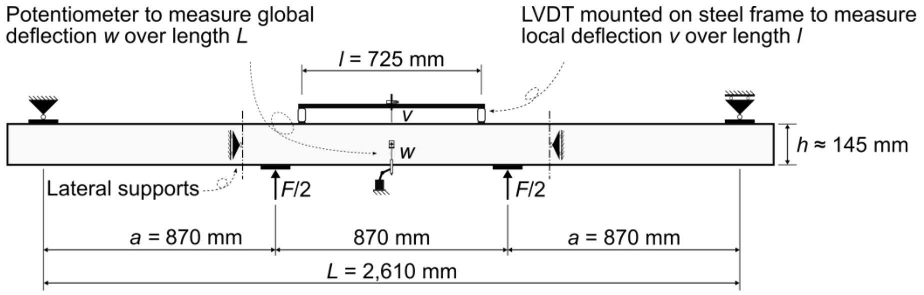

Figure 2: Four-point bending test set up based on EN 408 (2010) to determine bending strength (f_m), local MOE ($E_{m,l}$) and global MOE ($E_{m,g}$)

The 2D strain field on the surface of a randomly selected unmodified board (in this case board number 24) was recorded by a non-contact optical deformation measurement system. The board was loaded non-destructively in a four-point static bending test using a similar set up as described above. The measurement area included one flat side of the board with a length of roughly 400 mm that was positioned between the load points in the bending test. This area contained two arris knots and a smaller round face knot in the tension zone, and a round face and edge knot in the compression zone (Figure 3a). The determination of strain fields was based on digital image correlation (DIC) using the ARAMIS™ software (GOM mbH 2007). An overview of the test set up is shown in Figure 3b. After testing, the longitudinal (ε_x), lateral (ε_y) and shear (ε_{xy}) strains on the board's surface were calculated by the ARAMIS™ software. An extensive description of the herein used method was given by Oscarsson *et al.* (2012).

After the non-destructive tests, all 32 boards were modified on industrial scale according to the ThermoWood® process (max. 212°C/3h, total duration 3 days). Thermal modification was performed at Stora Enso's treatment facility in Launkalne, Latvia. Subsequently, the above described tests were repeated on the same set of boards after thermal modification, *i.e.* the modified boards (see Figure 1). This time, all 64 boards (control and modified) were bent to failure to obtain f_m [MPa] by Eqn. 3 assuming linear elastic material behaviour:

$$f_m \text{ [MPa]} = \frac{M_{\max}}{W_{\mathrm{el}}} = \frac{\frac{1}{2}aF_{\max}}{\frac{1}{6}th^2} \qquad (3)$$

where W_{el} is the elastic section modulus [mm^3] calculated using t and h measured at mid-span, M_{max} is the maximum internal bending moment calculated as the product of a and $F_{max}/2$, and F_{max} is the maximum applied load during testing. In addition, MC of each board was now obtained directly after testing by using the oven-dry method as described in EN 13183-1 (2002). Since properties were determined on the same board before and after modification, an independent t-test and two-tailed f-test were used to evaluate differences in mean values and standard deviation of the different properties, respectively. Simple linear regression was applied to study the relationship between boards' bending properties. The statistics were performed in Matlab®.

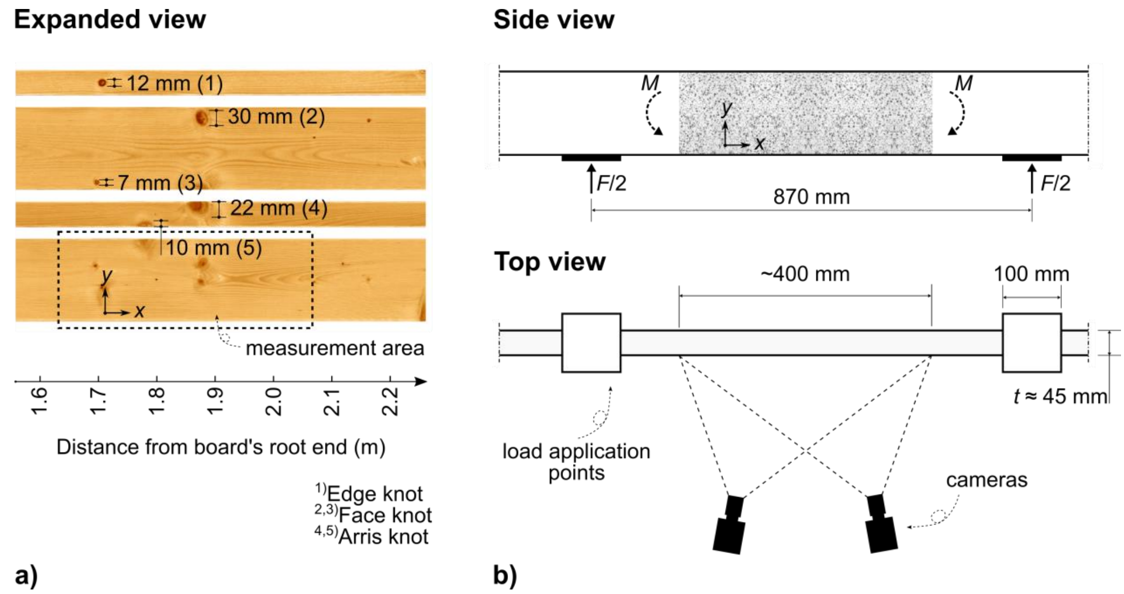

Figure 3: Test set up for strain field measurement on board no. 24: a) measurement area on one side of the board and b) set up of cameras for DIC measurement (note that the illustrated moment M is an internal bending moment)

RESULTS AND DISCUSSION

Static bending properties

The results in Table 1 show that $E_{m,g}$ was 11.6% higher after modification, whereas the difference in $E_{m,l}$ (*i.e.* 5.2%) was statistically not significant. The bending strength was significantly reduced after modification, *i.e.* f_m was 38.5% lower. It should be noted that the bending strength of the unmodified boards in Table 1 was obtained from the control boards (Figure 1). The magnitude of the described differences depend on the process conditions (Militz and Altgen 2014), and are somewhat in line with what was shown previously by Widmann *et al.* (2012) for TMT of beech. Standard deviations of the bending properties listed in Table 1 remained on a similar level after modification.

Table 1: Mean value ±standard deviation (coefficient of variation) for properties of unmodified and modified boards

Property	unmodified	modified	t-test^{b}	f-test^{b}
MC [%]	11.2 ±1.1 (9.7%)	4.6 ±0.6 (12.7%)	$29.80^{<0.001}$	$3.51^{<0.001}$
ρ [kgm^{-3}]	473 ±40 (8.4%)	436 ±34 (7.9%)	$3.88^{<0.001}$	$1.34^{0.428}$
$E_{m,g}$ [MPa]	11,857 ±1,421 (12.0%)	13,238 ±1,835 (13.9%)	$3.31^{0.002}$	$0.60^{0.167}$
$E_{m,l}$ [MPa]	13,282 ±1,835 (13.8%)	13,970 ±1,934 (13.8%)	$1.44^{0.156}$	$0.90^{0.776}$
f_m [MPa]	46.7 ±10.9 (23.3%)^{a}	28.7 ±8.3 (29.1%)	$7.32^{<0.001}$	$1.70^{0.15}$

^{a}*Values for bending strength (f_m) that are presented were obtained from the control boards (i.e. the mirror boards of the 2X-log sawing pattern),* ^{b}*test-value*$^{p\text{-}value}$

Linear regression analyses shown in Figure 4 between f_m of the modified boards and MOEs of the unmodified and modified boards, respectively, illustrate that bending strength of TMT can be predicted by employing MOE as indicating property (*IP*). This finding confirms results that were shown previously by Bengtsson *et al.* (2002) for TMT of Norway spruce and Scots pine (100 boards in each sample set). In addition, the results included herein show that the *IP* can be determined on the unmodified and modified boards (*i.e.* before or after modification).

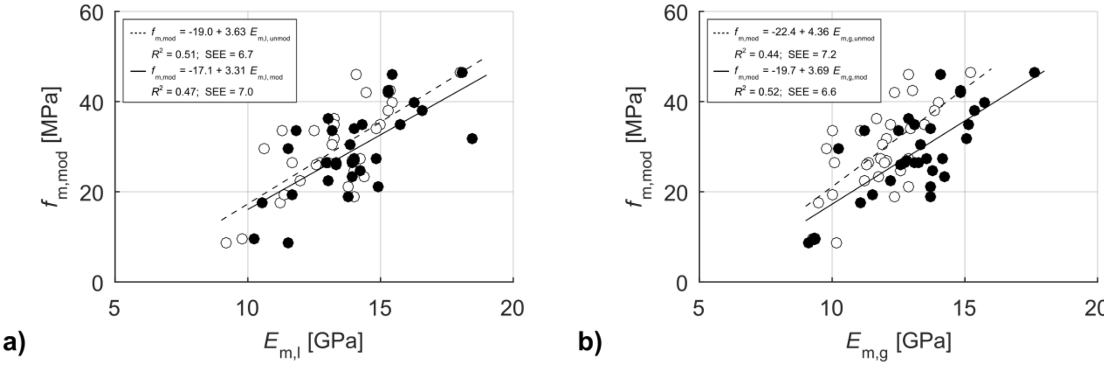

***Figure 4:* Relationships between f_m of the modified boards, and a) $E_{m,g}$ and b) $E_{m,l}$ of the unmodified (non-filled symbols) and modified boards (filled symbols)**

Strain fields around knots

The distribution of strains on the surface of a board before and after modification is shown in Figure 5. In general, these results are in line with previous measurements of strain distributions around knots in (unmodified) Norway spruce timber (Oscarsson *et al*. 2012). When looking in detail, large similarities can be observed between the unmodified and modified board for each type of strain. In the tension zone, higher values of ε_x were visible around the two arris knots, both before and after modification. In the compression zone, higher values of ε_x were visible around the edge knot, whereas the face knot did not lead to higher surface strains on this side of the board (note that the face knot was located on the other side of the board, *i.e.* the bark side). Although these similarities, it seemed that longitudinal strains (ε_x) around knots were somewhat higher after modification, but within the levels of loading examined herein these differences remained small. Similar observations were made for lateral (ε_y) and shear (ε_{xy}) strains. It is therefore likely that not only the global stiffness (*i.e.* determined over *L* and *l*), but also the local stiffness around knots is to a limited degree influenced by thermal modification.

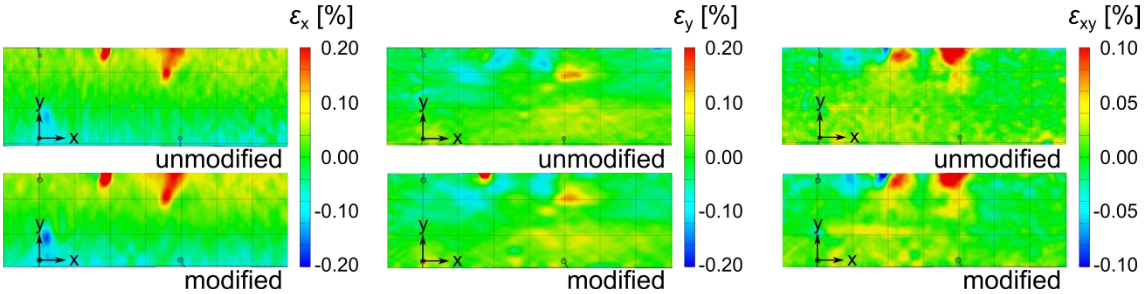

***Figure 5:* Contour plots for longitudinal (ε_x), lateral (ε_y) and shear (ε_{xy}) strains on the board's surface measured before and after modification on a board loaded with a bending moment of 1.31 kNm**

CONCLUSIONS

This study showed that the stiffness of thermally modified timber (TMT) of Norway spruce that was measured in a four-point bending test increased slightly (5-10%) due to the modification process. Although the bending strength was reduced up to approx. 40% by thermal treatment, linear regression analyses demonstrated that bending strength of TMT can be predicted by employing modulus of elasticity (MOE) as indicating property. Strain field measurements on the surface of one board loaded in bending showed high levels of strain around knots before and after modification. However, within the herein examined load levels it can be concluded that thermal modification had no influence on the quantity and distribution of strains within knotty areas. It is therefore likely that not only the global stiffness, but also the local stiffness around knots, is influenced to a limited degree by thermal modification.

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Thermomechanical (TM) treatment of beech wood (*Fagus sylvatica* L.) to substitute Indian rosewood (*Dalbergia latifolia* ROXB.) in musical instruments - mechanical and acoustic properties

Tobias Dietrich[1], Dr. Mario Zauer[1], Robert Krüger[1],
Prof. Dr. André Wagenführ[1]

[1]TU Dresden, Institut für Naturstofftechnik, 01062 Dresden, Germany [email: tobias.dietrich@tu-dresden.de]

Keywords: Densification, electric bass guitar, fingerboard, modal analysis, set recovery

ABSTRACT

THM (thermo-hydro-mechanical) or TM (thermo-mechanical) treatment of wood is a well-known process with different processing technologies and different properties of the modified wood, always aiming to eliminate or reduce the set recovery of the densified wood (Parviz and Sandberg 2011). Since January 2017, all *Dalbergia* species are listed in the CITES Appendix II. Hence trading or commercial playing with acoustic- or electric guitars or bass guitars is much more complicated and there is an urgent need for substitution materials. Indian rosewood (*Dalbergia latifolia* ROXB.) is used for fingerboards or as back and side material of the guitar body due to their hardness, acoustic- and sorption properties. For a suitable substitution material most important is to achieve a similar colour compared to Indian rosewood due to the modification.
Therefore European beech wood (*Fagus sylvatica* L.) was modified in a three-step TM process:

- Steaming (Plasticization)
- Densification (Increasing mechanical and acoustical properties)
- Thermal modification (Fixation of the shape, advanced sorption behaviour)

Densification parameters where chosen to achieve similar densities like common used Indian rosewood. Thermal modification was carried out at 190°C, 200°C, and 210°C.
After measuring basic properties, planks of densified beech wood in fingerboard dimensions where finally thermally treated at 200°C and bass guitars where manufactured for playing test with musicians. Results show, that set recovery is reduced due to the thermal modification and can almost be eliminated at 200°C. Dynamic young`s modulus is increased while acoustical damping is reduced to values comparable to Indian rosewood.

INTRODUCTION

Fingerboards used for musical instruments like guitar and bass guitar are mostly made out of Indian rosewood (*Dalbergia latifolia* ROXB.) Beside its outstanding mechanical properties, good dimensional stability, hardness and wear resistance, the color and texture is a main factor to uses this wood species. Due to overexploitation, Indian rosewood and other *Dalbergia* species are listed as endangered in the IUCN (International Union for Conservation of Nature) red list. Consequently, at the 17th CITES Conference (convention on international trade in endangered species) all *Dalbergia* species which were not listed in CITES appendix 1, were listed on CITES appendix 2 since 01.01.2017. Hence trading *Dalbergia* species is strongly limited under special conditions and under strict control mechanism. Besides using other tropical hardwoods as tone woods which are not listed in CITES, the most sustainable solution is using domestic wood species from sustainable forest management. Compared to the commonly used tropical hardwood species, European species are not reaching the dark colour and the required mechanical and acoustical properties without a thermal modification (Sproßmann 2017) or a chemo-mechanical modification (Dietrich 2014).

Krüger *et al*. (2018) thermally modified different European fruit species at 160°C for 8h as potential alternative to Indian rosewood for the use in classical guitars. The results show, that mechanical properties like MOE, MOR and Brinell hardness as well as swelling behaviour and acoustic attributes like damping can be improved to use thermally modified European fruit species for guitar making.

Zauer *et al*. (2016) also showed that the acoustical and mechanical properties of thermally modified European beech improve significantly at relatively mild (160°C) temperatures. Modulus of elasticity (MOE) increased while the damping behaviour decreased by 26% compared to untreated beech.

A proper substitution to Indian rosewood for fingerboards in terms of equal mechanical and acoustical properties was not found by these two studies. Only a higher density of European wood species, comparable to Indian rosewood, can lead to these equal properties. This can be done by reducing the porosity in a compression process under suitable moisture and temperature conditions. There have been reported several methods for compression of solid wood over the last decades (Seborg *et al*. 1956; Inoue *et al*. 1993; Morsing 2000; Kamke 2006). They are generally composed of compressing the wood perpendicular to the grain between heated metal plates to the desired thickness and fixing the deformation in the compresses state. One way to achieve a permanent fixation and to avoid moisture induced spring back is a thermal modification which reduces the wood hygroscopicity due to degradation of hemicelluloses (Parviz 2011, Dwianto *et al*. 1999). Morsing also reports of a rearrangement of cross-links within the microfibrills and between cell wall polymers which releases the inner stress created during compression (Morsing 2000). Such treated wood is called thermomechanical (TM) treated wood. TM treatment might be a promising method for using domestic wood species as substitute for fingerboards in musical instruments. Densification leads to improved mechanical and acoustical properties while the thermo treatment improves dimensional stability, permanent fixation and the desired dark colours. Since there are no studies about the suitability of thermomechanical treated wood for the use in musical instruments, this study will deal about the changes of the mechanical and acoustical properties of such treated wood with the aim to achieve similar properties like Indian rosewood.

EXPERIMENTAL

Thermomechanical Treatment

European beech specimens clear of defects with horizontal annual growth rings with the dimensions 200x35x10mm³ (LxTxR) were oven dried at 103°C and afterwards conditioned at relative humidity (RH) 65% and 20°C until reaching equilibrium moisture content. To reduce the required pressing force, all samples were steamed prior to densification by saturated hot steam at 102°C for 1h. Densification in radial direction was done immediately in a hot press at 100°C between preheated (100°C) metal plates which can be fastened with screws. Compression ratio was calculated and set to 25% to reach a density around 900kg m^{-3}, comparable with superior qualities of Indian rosewood. Compression was carried out at a constant speed, at 2mm/min. Test showed, that the density profile in compression direction is almost even at this speed. After compression the samples were conditioned at RH 65% and 20°C before opening the steel plates. Respectively twelve of the small and two big samples were thermally modified by a patented process in a flexible silicone bag at 190°C (3h), 200°C (2h) and 210°C (2h) in a laboratory oven at 10K h^{-1}. Prior to the modification, the air was removed by a vacuum at 5kPa for 5 minutes. Fastened steel plates ensured that internal forces cannot be released during the thermal modification. After the thermal modification all samples were oven dried again to calculate the mass loss. Two Fingerboard sized planks with 700x80x10mm³ (LxTxR) were densified as described but were modified at 200°C for measuring dynamic and acoustic properties.

Measurement methods

Set recovery and Anti-Swelling-Efficiency was determined on the small samples. Experimental modal analysis and attack and sustain analysis were determined on modified fingerboard sized samples as well as on a manufactured bass guitar.

Set Recovery

For measuring the set recovery, a cyclic water storage and drying process according to Inoue *et al*. (1993b) was conducted on twelve samples with the dimension of 40x28x7.5mm³ (LxTxR), which were cut out of the compressed samples. For that purpose, the oven dried samples were exposed to a vacuum of 10kPa for 30 minutes. Then water at 20°C was added to the samples for 24 hours. Afterwards, the samples were dried in an oven again. This procedure was repeated three times. The set recovery R_S, was determined after Eqn. 1:

$$R_S\ (\%) = [(l_r - l_c)/(l_0 - l_c)] \times 100 \qquad (1)$$

Where l_r is the radial thickness under oven-dried conditions after each water storage and l_0 and l_c are the oven-dried radial thicknesses before and after compression.

Anti-Swelling Efficiency (ASE)

The swelling coefficient S was determined (Eqn. 2) from the last cycle of the set recovery measurements to avoid an influence of the radial set recovery on the ASE.

$$S\ (\%) = [(V_{WS} - V_{OD})/V_{OD}] \times 100 \qquad (2)$$

Where V_{WS} is the water saturated volume and V_{OD} the oven dry volume. ASE was calculated after Eqn. 3 with the swelling coefficient from unmodified (S_U) and modified (S_M) wood.

$$ASE\ (\%) = [(S_U - S_M)/\ S_U] \times 100 \qquad (3)$$

Experimental modal analysis (EMA)

Fingerboard sized modified (200°C) planks were measured by experimental modal analysed according to Sproßmann *et al* (2017) with free-free boundary conditions. Dynamic Young´s modulus (E´), internal friction (Q^{-1}) and dynamic shear modulus (G`) were measured.

Acoustic properties

To determine acoustic properties, one bass guitar with a TM Beech 200°C treated plank was build and tested with a plucking test similar to the test reported by Zauer *et al.* (2016).
Mass loss, equilibrium moisture content, sorption isotherms, Brinell hardness, bending properties and colour were also tested, but results are not shown in this paper.

RESULTS AND DISCUSSION

Set recovery (R_S) and Anti-Swelling-Efficiency (ASE)

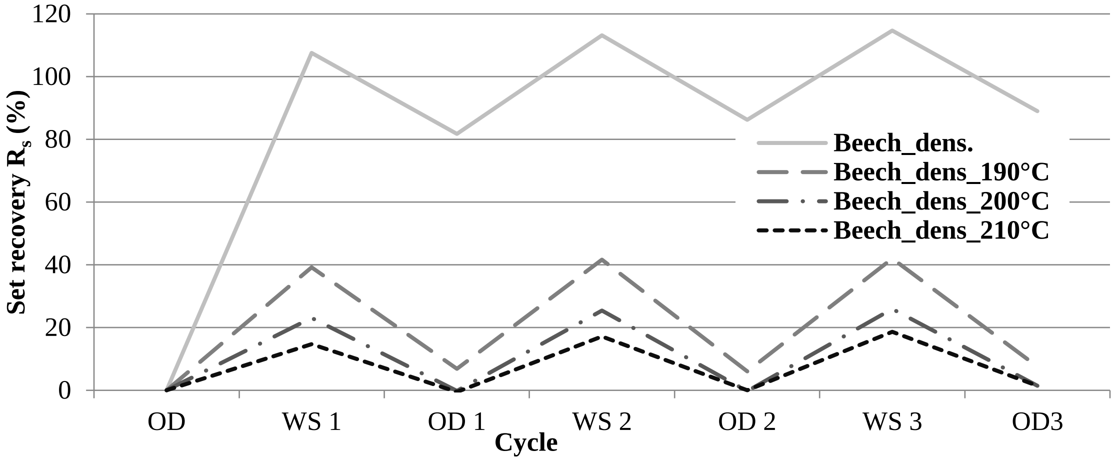

Figure 1: Set recovery of densified samples unmodified and thermally modified at 190°C,200°C and 210°C during three oven dry and water saturated cycles (OD, WS)

Set recovery (see Figure 1) is significantly reduced due to the thermal modification. Unmodified densified samples recovering almost completely to their original radial thickness. At 190°C, set recovery is reduced to 6.8 % increasing to 7.3% after the third harsh water cycle. From 200°C and above, set recovery is eliminated even after three water cycles. With a thermal treatment above 200°C, moisture induced springback can be eliminated and the densified wood is stabilised.

ASE (see Table 1) is decreasing at 190°C to -22 % instead of increasing as expected due to the thermal modification. Due to a greater radial swelling compared to reference beech resulting from the densified folded structure associated with a higher radial strain,

Table 1: ASE, tangential (α_t) and radial (α_r)swelling of unmodified and TM beech, median m and standard deviation SD

		ref	190°	200°C	210°C
ASE [%]	m	0	**<u>-21.8</u>**	**6.5**	**22.2**
	SD	0	3.1	3.3	3.8
α_t [%]	m	**12.2**	**8.9**	**7.0**	**6.0**
	SD	1.2	0.2	0.4	0.3
α_r [%]	m	**7.8**	**<u>15.7</u>**	**12.1**	**9.6**
	SD	0.3	0.5	0.5	0.6

ASE is decreased and only increased at 210°C. Even at 210°C, the radial swelling is slightly higher compared to unmodified samples. As expected, tangential swelling is significantly reduced with increasing temperature.

EMA

Results from the EMA on fingerboard planks densified and thermally modified at 200°C are shown in Table 2. Due to the densification and thermal modification, the dynamic modulus and shear modulus are significantly increased compared to reference beech. The obtained values are equal or even higher than Indian rosewood. Damping is reduced to a value comparable to

Indian rosewood. Due to the shear forces on the neck of electric bass guitars by the tension of the strings, a high shear modulus as well as a high dynamic modulus is important and TM Beech can fulfil this requirement.

Table 2: Dynamic young's modulus E', dynamic shear modulus in LR plane G_{LR}', damping coefficient Q^{-1} of densified and thermally modified beech wood, ref. beech and Indian rosewood, median m and standard deviation SD

		TM Beech (930 kg m^{-3})	Beech ref. (675 kg m^{-3})	Indian rosewood (781 kg m^{-3})
E' [GPA]	**m**	**24.9**	**16.9**	**14.6**
	SD	0.7	0.5	2.1
G_{LR}' [GPa]	**m**	**2.0**	**1.0**	**1.7**
	SD	0.1	0.1	0.3
Q^{-1} [10^{-3}]	**m**	**6.25**	**7.60**	**6.03**
	SD	0.33	0.82	0.40

Attack and Sustain

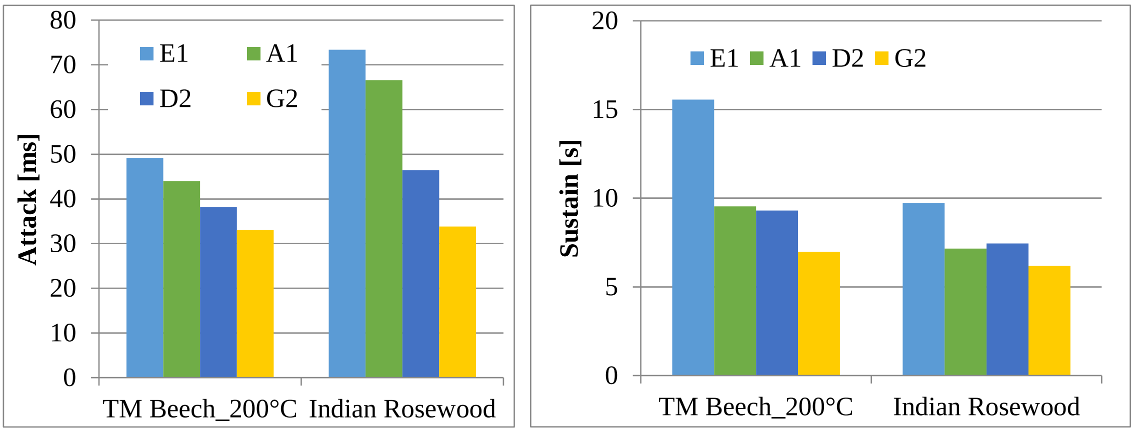

Figure 2: Attack and sustain measured on a bass guitar with a TM Beech 200°C fingerboard compared to a bass guitar with an Indian rosewood fingerboard, E1,A1,D2,G2 single strings

Attack, describing the time during which the sound volume grows from plucking the string to a maximum level is reduced on every string below the level of Indian rosewood. Sustain, describing the time during which the sound remains before it becomes inaudible and begins when attack is reached is increased above the level of Indian rosewood. Both values indicating, that TM Beech can have a responsiveness and sound behaviour equal to Indian rosewood. Blind playing test revealed that musicians cannot hear differences between TM Beech fingerboards and Indian rosewood fingerboards. The appearance of such modified wood with the pronounced ray vessels is a visual disadvantage compared to rosewood and is not adequate for the musicians.

CONCLUSIONS

Densification and fixation by thermal modification of European beech wood leads to an substitution material for Indian rosewood. While the sound quality, the colour and the sorption properties are comparable with Indian rosewood, the appearance of such modified beech is not always accepted by musicians. That´s why in further studies other European species will be treated and tested. In terms of colour, set recovery and machinability, thermal modification of densified beech at 200°C is a good compromise.

ACKNOWLEDGEMENTS

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4 years field study in contact with the ground of thermomodified Scots pine sapwood

Andrzej Fojutowski[1], Andrzej Noskowiak[2] and Aleksandra Kropacz[3]

[1,2,3]Wood Technology Institute,Winiarska str. 1, 60 654 Poznań, Poland
[1][email: fojutowski@itd.poznan.pl]; [2][a_noskowiak@ itd.poznan.pl]; [3][a_kropacz@ itd.poznan.pl]

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ABSTRACT

The Scots pine (*Pinus sylvestris* L.) is very often use in constructions and in many other products. The sapwood of Scots pine is considered to be much more less durable than heartwood as regards to biological and physical destroying factors. Those difference may limit the scope of Scots pine wood applications in difficult conditions *e.g.* as terrace boards. The thermomodification is a process that can improve some of the unfavourable properties of wood, including its durability. The thermomodification effectiveness in terms of increasing the durability of wood is determined by laboratory studies (EN 350, EN 599-1), which attempts to mimic the action of biotic and abiotic factors, especially weather. It do not fully meet to the complexity of natural conditions and the effects of their coexistence. So, EN 252 field test in ground contact in terms of direct impact of atmospheric and biological factors, is mostly use to determine the durability of wood. The aim of this research was to identify the resistance of thermomodified Scots pine sapwood after 4 years of contact with the ground according to EN 252 method, in comparison to natural twin wood of this species. The thermomodification of wood was carried out in an industrial plant, in an open system with temperature to 210° C, in air. The equilibrium moisture content, density, bending strength and MOE in bending of tested thermowood decreased as effect of thermomodification in comparison to natural wood, but the compressive strength along the grain increased. Test of wood in ground contact was carried out on field test formed in 2010 by the Wood Technology Institute on Jarocin Forest District lands. The average degree of attack assessment of natural pine wood was 3.17 (above rating 3 *i.e.* limit of strong attack) and wood softening was average 15.1mm, but for thermo-pine sapwood average degree of attack was smaller=2.76 *i.e.* below the limit for grade 3 - strong decay and the wood softening was average only 8.4mm. The 4 years field exposition indicate that thermomodified Scots pine sapwood is decomposed in ground contact slower and less deeply than the natural wood of this species.

INTRODUCTION

The Scots pine (*Pinus sylvestris* L.) takes in Poland about 58% of forest area and its wood dominate in industrial use (Forest …2017). The wood of the species is very often use for many purposes as building – structural timber, aircraft timber, floorings, railways sleepers, marine sawnwood, transition poles, fence and many other products. It has two anatomical zones of different properties: sapwood and heartwood. The sapwood of Scots pine, based on data derived from the results of laboratory or field tests simulating natural weathering situation, is considered to be much less durable than heartwood as regards fungi, insects destroying wood, contact with ground and/or water and weathering conditions. The heartwood of Scots pine is classified to moderately or slightly durable materials (durability class DC 3 – 4) according to European standard (EN 350), but the sapwood of Scots pine belongs only to durability class DC 5 – not durable. Those difference may limit the scope of Scots pine wood applications in conditions of wood exposition on wood destroying agents, *e.g.* as terrace boards. This is the reason for the restrictions on the use of this wood in open air and in ground contact and the need to increase its durability for use in such conditions. The wood in contact with ground and/or sea or fresh water *i.e.* respectively 4 and 5 use classes conditions is most exposed to the damaging effects of atmospheric and biotic factors. The scope of using the not enough durable wood in consequence become smaller. The impregnation of wood with biocides is one of the widely used methods of increasing the durability of wood. The method may, however, cause environmental hazards. Biocidal Products Regulation [BPR 2012] require limitation of the use of chemical substances for wood impregnation whenever it is possible without exposing the product to premature loss of desired properties. The resistance of wood to wood-decaying fungi from the class Basidiomycetes as well as dimensional stability may be increase by the thermomodification of wood, without use of biocides (Militz and Hill 2005).So, besides of using biocides of possible not good influence to environment, the thermal modification may be consider a more environment friendly process that can improve some of the unfavourable properties of wood, including its durability. The reduction of the amount of hydroxyl groups of cellulose and hemicelluloses, which are involved in oxidative degradation, fungal decay, and the processes of water absorption and desorption by wood are the cause of the improving of wood properties (Militz 2002). It was however found that the thermomodified wood is still quite strongly vulnerable to attack of filamentous fungi that cause moulding of wood. The same group of fungi may cause soft rot of wood with a prolonged period of favorable conditions for their growth (Fojutowski *et al*. 2009). It is expected that the species or zones of wood, with low natural biologic durability thanks to thermomodification can increase its durability and, as result, find wider application in the buildings and in terms of contact with the ground conditions. The effectiveness of the thermomodification in terms of increasing the durability of wood is determined by laboratory studies (EN 350, EN 599-1), which attempts to mimic the action of biotic and abiotic factors, especially weather. The laboratory conditions however do not fully meet to the full complexity of natural conditions and the effects of their coexistence. So, field test in ground contact in terms of direct impact of atmospheric and biological factors, are mostly use to determine the durability of wood [EN 252]. The test should be extended to the wood for at least five years.

The goal of the study was to determine the efficacy of thermomodification of Scots pine sapwood in increasing its resistance in ground contact after 4 years of contact with the ground according to EN 252 method, in comparison to natural twin wood of this species, for the assessment of possibility of extension its use in construction.

EXPERIMENTAL

Material and its preparation

Twin (directly adjacent to side measuring 500 × 50 mm) samples size of 500 (L) × 50 (R) × 25 (T) mm in number 30 pieces of natural and 30 pieces of thermally modified Scots pine (*Pinus sylvestris* L.) sapwood were prepared. The thermally treatment was carried out in an industrial plant, in an open system under conditions of temperature to 210° C, in air. After heat treatment the wood samples were selected to test (eliminating cracks, warping).

The tests of physical properties of prepared wood samples wood has shown that equilibrium moisture content, density, bending strength and MOE in bending of wood decreased as effect of thermomodification. The compressive strength along the grain however increased (Fojutowski *et al.* 2015).

Methods

The samples were exposed to weathering and all biological factors in the field test in contact with the ground, according to requirements of the standard EN 252. The properties of ground of field test were also determined (Jacobs *et. al.* 2014). Before samples were buried in the ground to half of their length, they had been air-conditioned in the standard climate, i.e. at 20±1° C and 65±5% relative humidity.

The main rating system for the assessment of samples degradation followed the EN 252 standard:

0 – no attack – no change (if only a change of colour is observed, it shall be rated 0),

1 – slight attack – superficial degradation, limited intensity, softening of the surface (< 2mm),

2 – moderate attack – softening to ≥ 2 mm over a surface of ≥ 10 cm^2 or 5 mm over < 1 cm^2,

3 – strong attack – decay of ≥ 3 mm over a surface ≥ 25 cm^2 or softening to ≥ 10 mm over more limited area,

4 – failure – impact failure of the samples in the field.

The evaluation and the assessment of the condition of the samples was supplemented with some additional observations concerning the presence of fungi on the underground part of the stakes (samples) and/or the algae/mould presence on the above-the-ground part of the stakes *etc.* The climate data were also recorded.

RESULTS AND DISCUSSION

Figure1 presents climatic conditions (temperature and precipitation) on the test field during the last year of the test. The average yearly values of the temperature was 11.0°C (daily minimum – 16.0°C to maximum + 35.5°C) and average precipitation referenced to days with precipitation was 6.2 mmH$_2$O (daily, highest 42.0mmH$_2$O and smallest 0.5mmH$_2$O). Rainfall was 510 mm *i.e.* close to long-term average value.

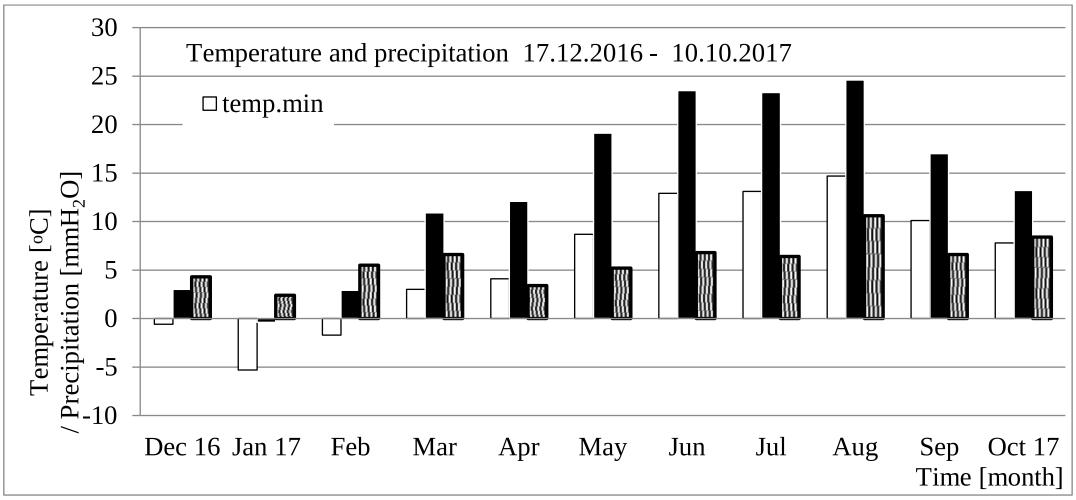

Figure 1: The monthly average minimum and maximum temperature and precipitation on the field test area

The stated average degree of attack assessment (Table 1 and Table 2) of natural pine wood was 3.17= the state of slightly more than attack known as a strong attack (rating 3). The deep of wood softening was about 15 mm, and 90% of samples characterized by softening of the wood depth over of 5 mm. Most samples (97%) showed on the surface the presence of moulds, and algae 93%.

The average degree of evaluation samples of thermo-pine sapwood, was smaller=2.76; *i.e.* below the limit for grade 3 - strong decay; the presence of moulds were found on only 14% of samples, while algae occur on all (100%) of samples; the depth wood softening was average 8.4mm. Tested for comparison natural Poplar wood has been destroyed stronger – 3.77 degree (PN-EN 252: very strong attack (failure) - grade 4, and strong - grade 3), including 20 samples were broken, and the depth of softening generally ranged from 15 - 20 mm, indicates the advanced wood decay. All samples turned greyish, cracks occurred on the samples foreheads.

Table 1: Assessment of attack caused by microorganisms - 4 years exposition of test stakes - EN 252

Properties	Values	Scots pine sapwood	
		Natural	Thermo
Rating of wood attack	Minimum	3.00	2.00
	Mean	3.17	2.76
	Maximum	4.00	4.00
Depth of wood softening [mm]	Minimum	5.0	3.0
	Mean	15.1	8.4
	Maximum	20.0	20.0

Table2: The assessment of degradation of the Scots pine sapwood test samples – condition after 4 years exposition in contact with ground - EN 252 test.

Mean rating of tested wood after 4 years of field exposition		
Symptoms	**Scots pine sapwood**	
	natural	**thermo**
Fungi at underground part [%][a]	43	37
Evidence of moulds at over ground part [%][a]	97	14
Evidence of algae at over ground part [%][a]	93	100

[a] *percentage of samples units with common symptoms*

The ranking of evaluations changes is presented in Table 3. The evaluations of thermo Scots pine sapwood after each of tested years are lower than that of natural Scots pine sapwood. The biggest difference occurred after 4 years.

Table 3 The assessment of degradation degree of natural and thermo modified Scots pine sapwood in contact with the ground according to EN 252 – exposition on the test field in Jarocin Forest District in the period 2014-2017

Scots pine sapwood (*Pinus sylvestris* L.)									
natural					thermally modified				
Average rating	Evaluation after [year]				Average rating	Evaluation after [year]			
	1	*2*	*3*	*4*		*1*	*2*	*3*	*4*
	1.30	2.70	2.90	3.17		1.17	2.57	2.70	2.76

CONCLUSIONS

The results after four years of field exposition, indicate that thermomodified Scots pine sapwood is decomposed in ground contact slower, than the natural wood of this species. The thermo- and natural pine sapwood have shown clear signs of decay after four years of exposure in the ground, however thermowood is decayed less deeply.

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Mineralization of wood with calcium oxalate

Tom Franke[1] and Thomas Volkmer[1]

[1]Bern Univerity of Applied Sciences- Architecture, Wood and Civil Engineering; Institute for Materials and Wood Technology, Soluthurnstrasse 102, CH-2504 , Biel, Switzerland
[email: tom.franke@bfh.ch]
[email: thomas.volkmer@bfh.ch]

Keywords: durability, fire resistance, mineralization, wood modification

ABSTRACT

European beech and Scots pine were impregnated in a two-step process with aqueous solutions of potassium oxalate and calcium chloride, successively. The two compounds shall react *in situ* to the water-insoluble salt calcium oxalate and the reaction by-product potassium chloride. In order to assess the treatability of the selected wood species, the solid uptake after the first impregnation and after the treatment was examined. The fixation of the precipitated salts was determined in leaching tests according to the European standard EN 84. Resistance against wood destroying fungi was determined in a laboratory test according to the European standard EN 113. Flammability of mineralized beech was tested following the ISO 11925-2. The treatment indicates an improved resistance against wood destroying fungi. However, high amounts of leached out chemicals prior the test leads to a pronounced reduction of this effect. Results from flammability tests indicate improved resistance against fire due to the mineralization.

INTRODUCTION

Mineralization of wood is a natural process which occurs during fossilization of wood. It is a long-term process and describes the accumulation of non-organic materials, such as silicon, calcium carbonate or phosphor, in the wood resulting in a preservation of wood (Buurman 1972). Until today, various approaches have been developed to achieve artificial mineralized wood to overcome various drawbacks of wood. Artificial mineralization based on silicon was widely investigated and a comprehensive amount of formulations in combination with wood were investigated (Mai and Militz 2004a,b).

Another approach of artificial mineralization of wood is the *in situ* precipitation of water-insoluble salts inside wood to obtain a material with improved properties, e.g. improved fire retardancy. Merk (2016) precipitated calcium carbonate in wood and showed an improved fire retardancy caused by this treatment. Investigations by Khelfa *et al.* (2013) evidenced improved fire retardancy of $MgCl_2$ and $NiCl_2$ treated birch.

In this study calcium oxalate (CaOx) shall precipitated into European beech (*Fagus sylvatica*) and Scots Pine (*Pinus sylvestris*). The water insoluble salt CaOx is found in nature e.g. as kidney-stones or in various plants such as rhubarb *(Rheum rhabarbarum*) as protection against herbivores. Furthermore, CaOx is known to be a by- product of the wood degradation process caused by copper-tolerant wood-destroying fungi (Stephan *et al.* 1996).

This study aims to investigate the treatability of the selected wood species, as well as the effect of the treatment due to the biological resistance against wood destroying fungi and the behaviour when exposed to fire.

EXPERIMENTAL

Materials and chemicals

The wood species European beech (*Fagus sylvatica)* and Scots pine (*Pinus sylvestris*) were selected for the study. Precipitation of CaOx and the reaction by-product potassium chloride (KCl) is initiated according to Eqn 1. The reactants potassium oxalate monohydrate (KOx) (99 % purity) and calcium chloride hexahydrate ($CaCl_2$) (98 % purity) were obtained from Sigma Aldrich®.

$$C_2O_4K_2 + CaCl_2 \quad \rightarrow \quad C_2O_4Ca + 2KCl \qquad (1)$$

The reactants were diluted in deionized water in the ratio given in Table 1. The ratio was selected in accordance to stoichiometry calculations to ensure maximum conversation of the reactants inside the wood.

Table 1: Mixing ratio reactant : H_2O (w : w) and ratio of the reaction product

Reactant 1 $C_2O_4K_2 : H_2O$	***Reactant 2*** $CaCl_2 : H_2O$	***Product*** $C_2O_4Ca + 2KCl$
1 : 2.8	**1 : 2.1**	**1 : 1.2**

Impregnation

The general mineralization process was performed according to Figure 1. The reactants were impregnated into the wood in a two-step process, successively. The impregnation of a single reactant consists in a vacuum – pressure cycle and was carried out in an autoclave at 23 °C. After the 1st step, specimens were dried at room conditions to *appr*. 20% moisture content before impregnation of the 2nd chemical.

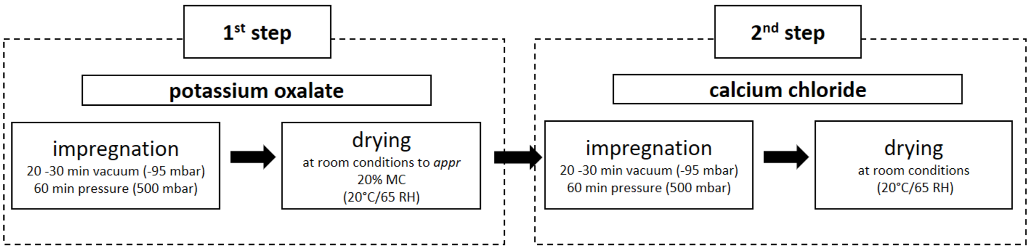

Figure 1: Treatment schedule of the two-step process for the mineralization of European beech and Scots pine to obtain CaOx.

Solid uptake, weight percent gain and fixation

The solid uptake after the first impregnation step, as well as the weight percent gain after the second impregnation step were determined based on the absolute dry weight according to Eqn 2. The absolute dry weight was determined in a kiln dry at 103 °C until constant weight.

$$\boldsymbol{WPG\ /Solid\ Uptake} = \frac{\boldsymbol{w_1 - w_0}}{\boldsymbol{w_0}}\ ;\ \% \qquad (2)$$

Where Solid Uptake is the theoretical uptake of the precipitated reactants after the first impregnation step and WPG is the theoretical uptake of the reaction products CaOx and KCl, respectively. Furthermore, w_1 is the absolute dry weight after each impregnation step in gram, and w_0 is the absolute dry weight before impregnation in gram.

Leaching

Leaching was performed for the purpose of estimating the fixation of CaOx and the by-product KCl in the wood, as well as accelerated ageing and leaching prior the biological tests. The leaching protocol follows the specifications noted in the European standard EN 84.

Biological tests

Mineralized beech specimens and their corresponding controls were tested against *Coriolus versicolor* and mineralized pine specimens and their corresponding controls were tested against *Coniophora puteana*. The fungal resistance of the treated wood was evaluated in two series of tests according to the European standard EN 113. In the 1st series, specimens were exposed without leaching prior the test, while in the 2nd series specimens were leached prior the test. Two treated specimens and one untreated control specimen was added to each flask. Overall 8 specimens for each treatment and 4 untreated controls were tested. Additionally, virulence of the test fungi was tested simultaneously. However, departing from the standard, the dimensions of the specimens altered ($50 \times 12 \times 15$ mm^3). Additionally, the time of incubation of the specimens exposed to the fungi was 11 weeks instead of 16.

Reaction to fire

Six mineralized beech specimens as well as six untreated beech specimens with the dimensions of $250 \times 90 \times 20$ mm^3 were tested and evaluated according to the standard ISO 11925-2. The flame was set with a metallic cylinder equipped with a cone-like point with an angle of 45°. It is positioned in the output of the lighter needle with the point *appr.* 1.5 mm below the edge of the sample (Figure 2). The length of the flame was 20 mm and the flux of air was 0.6 -0.8 m^3/s. The specimens were exposed to the fire for 105 sec. Subsequently, the time the wood stays burning after the flame is retired was recorded. Furthermore, the extend of the flame trace was measured after the test. Thereby, length and width of the flame trace was measured (Figure 2) and presented as the sum of both.

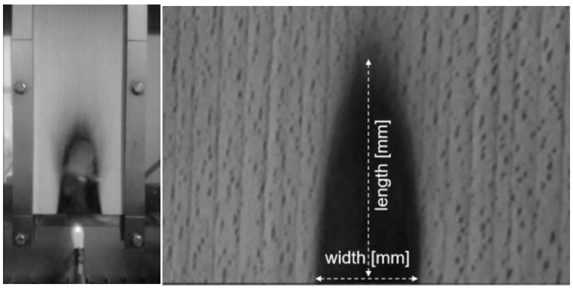

Figure 2: Preparation of the fire retardancy test (left) and measurement of the extend of the flame trace (right)

RESULTS AND DISCUSSION

The solids uptake after the first impregnation step, as well as the WPG after the 2nd step and after leaching is presented in Figure 3. The pine specimens display higher solid uptake compared to the beech specimens. It is assumed, that the lower density, and hence the higher porosity of pine leads to a higher uptake of the mineralization agents. After leaching, 32 % in pine respectively 12 % in beech of the mineralization agents are left over. The reaction by-product KCl is water soluble and thus, easily washed out. In contrast, CaOx is poorly water soluble. However, according to stoichiometry calculations (Table 1), a higher amount of chemicals was leached out than presumed. It is assumed, that the majority of the by-product KCl, as well as unreacted KOx and $CaCl_2$ leached out, while the CaOx is fixed relatively stable in the wood.

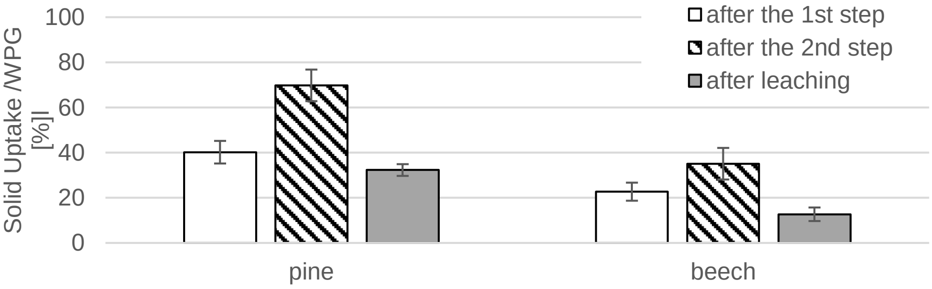

Figure 3. Solid uptake after the first impregnation step, the WPG after the second step as well as the WPG after leaching of CaOx mineralized pine and beech

Biological tests

The results for the biological tests are displayed in Figure 4. Tested against *Coniophora puteana,* the mineralized and unleached pine displays an average weight loss of 2.1%. Tested against *Coriolus versicolor*, the mineralized and unleached beech exhibits an average weight loss of 4.5%. At the same time, untreated pine exhibits a weight loss of 9.7% and untreated beech – 0.5%. After leaching, an average weight loss of 21.5% for pine and 15.4% for beech was measured. The weight loss of the untreated control specimens was also higher compared to the control specimens tested together with the unleached specimens (31.96 % for pine and 17.5% for beech).

The mineralized beech and pine specimens, which were not leached before testing indicates improved biological resistance with an average weight loss of less than 5%. Additionally, leaching of the unfixed precipitated salts inside the test flask might also contribute the fungi growth and hence, the relatively low weight loss of the control specimens. In particular, the chlorine might diffuse into the agar and inhibit the fungi growth. This might explain the poor weight loss even of the untreated controls.

In contradiction, leaching of the mineralized specimens prior the test exhibits higher weight losses of mineralized specimens, as well as for the control specimens. As shown in Figure 3 *appr.* 50% of the chemicals are washed out during leaching. As discussed before, it is assumed that the majority of chlorine is already leached out and thus, the impact to the fungi growth becomes less pronounced. This leads to a high weight loss of the controls, whereas remaining CaOX in the treated wood might serve as mechanical barrier that retards the fungi action.

However, more work hast to be done to strengthen this assumption. Furthermore, in the present study, virulence test for *Coriolus versicolor* displayed insufficient weight loss of 14%. According to the EN 113 a weight loss of more than 20% must be obtained to confirm sufficient virulence of the test fungi. Furthermore, the exposition was only 11 weeks instead of 16 and thus, the results for virulence test might be less than the required value. Nevertheless, the results provide a suitable indicator for the impact of mineralization of beech and pine against wood destroying fungi. However, due to the high leaching of the chemicals when exposed to water associated with a decrease of the durability, this treatment might not be suitable for outdoor applications.

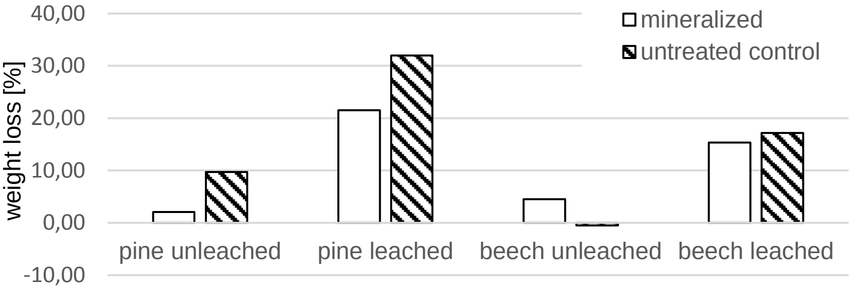

Figure 4 Weight loss of leached and unleached mineralized pine, and their untreated control caused by *Coniophora puteana* and weight loss of leached and unleached mineralized beech and their untreated control caused by *Coriolus versicolor*

Reaction to fire

The effect of the mineralization with $CaCl_2$ and KOx to obtain CaOx in beech regarding the behavior against fire is presented in Figure 5. The burning trace of the untreated beech samples is clearly bigger than the trace of the mineralized beech samples (Figure 5 a, c). Furthermore, the time the wood stays burning after the flame is retired is almost eliminated for the mineralized beech (Figure 5, b).

Inorganic salts are generally non-combustible. Thus, the results from the flammability tests evidence, that the treatment can improve the inflammability of beech wood. Additionally, the precipitated salts, and in particular chlorides, have a high hydrophilic effect resulting in a higher equilibrium moisture content compared to untreated wood (Furuno *et al.* 1992). This could also contribute the performance of the mineralized wood against fire. Interior applications with special requirements to inflammability might be a conceivable field of application for CaOx mineralized wood.

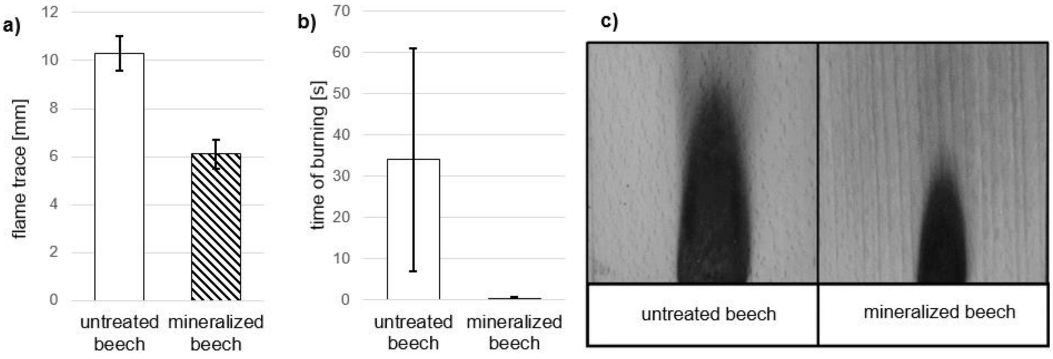

Figure 5 Fire behaviour of CaOx mineralized beech. a) flame trace b) time of burning after flame is retired c) images of the flame trace

CONCLUSIONS

The feasibility of an impregnation with $CaCl_2$ and KOx to obtain CaOx in Pine and beech was demonstrated. Following further conclusions can be drawn:

- A high uptake of the impregnation agents $CaCl_2$ and KOx into Scots pine and European beech indicates proper treatability of this wood species to obtain CaOx.

- A high amount of leached out chemicals was determined. It is assumed, that the majority of leached out chemicals is attributed to the by-product KCl, as well as unreacted $CaCl_2$ and KOx. However, more work is needed to strengthen this assumption
- The treatment can basically improve the resistance against wood destroying fungi. However, this effect becomes less pronounced after leaching.
- The flammability of the mineralized beech is improved compared to untreated beech by means of the flame trace and the time of burning after the flame is retired.

ACKNOWLEDGEMENTS

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Preparation of thin functional coatings on wood and WPC materials using atmospheric pressure plasma jets

Sven Gerullis[1], Andreas Pfuch[1], Florian Kettner[2], Katharina Plaschkies[2], Bernd Grünler[1], Mario Beyer[2], Gennadi G. Volokitin[3]

[1]INNOVENT Technology Development e.V., DE-07745 Jena [email: sg@innovent-jena.de]
[2]IHD Institut für Holztechnologie Dresden gemeinnützige GmbH, D-01217 Dresden

[3]TSUAB Tomsk State University of Architecture and Building, 634003 Tomsk Russia

Keywords: antimicrobial, atmospheric pressure plasma jet, thin functional films

ABSTRACT

The colonization of wood and wood-based materials by microorganism can cause aesthetic damage, negative impact on mechanical properties or even health hazards. This work investigated structural morphology, elemental composition and antimicrobial properties of thin (~50-200 nm) functional silicon oxide films deposited on wood using atmospheric pressure plasma chemical vapour deposition. By different plasma system modifications, it was additionally possible to embed active agents into the growing silicon oxide films. Investigations by X-ray photoelectron spectroscopy and depth profiling indicating the integration of active agents into the created silicon oxide film matrices. Moreover, the possibility to generate combinations of active agents in one layer could be demonstrated. Antibacterial investigations showed strong bactericidal properties for silver and copper as well as sufficient properties zinc-containing layers against *Escherichia coli*. Antimycotic effects on mould strains *Aspergillus niger*, *Paecilomyces variotii, Penicillium funiculosum* and *trichoderma viride* were low for films containing only one active agent. Significant improvements in activity were achieved by the combination of these active agents.

INTRODUCTION

In the last years a significant progress has been made in the field of plasma enhanced chemical vapour deposition processes under ambient pressure conditions. Especially with the broadened spectrum on commercially available plasma sources the industrial application of this technique is more and more addressed. It has been shown that functional thin films can be prepared successfully onto different substrate materials by using Atmospheric Pressure Plasma Jet (APPJ) technologies (Pfuch *et al.* 2010, Beier *et al.* 2013). Atmospheric pressure plasma treatments were realised on wooden materials by using dielectric barrier discharges e.g. with the aim to influence the wettability of the surface (Mahlberg *et al.* 1998, Wolkenhauer *et al.* 2007). Nevertheless, most of scientific work was focused on a pure plasma interaction with the wood surface, thus the preparation of certain functional thin films on wood-based materials using plasma polymerisation processes is quite unexplored.

Wood-based materials need regular maintenance and care of their surfaces to raise persistency against, for example climatic influences. One reason for this is that wood as a natural product is biologically degradable by bacteria and fungi (Rowell 2005). The biological degradation and the associated infestation by microorganism are adverse, because performance characteristics such as aesthetic appearance or mechanical properties can be lowered. Compared to conventional prevention methods such as wood impregnation or the application of active agent-containing primer systems, the atmospheric pressure plasma chemical vapour deposition (APP-

CVD) creates very thin active agent-containing films with total film thicknesses between ~50-200 nm. In contrast to conventional approaches, which try to modify the whole bulk material, it was attempted to apply only thin composite films containing active agents on top of the materials. Hence, larger quantities of antimicrobial agents can be saved in an economical and sustainable way.

EXPERIMENTAL

APP-CVD technology

Thin films on wood material were deposited using a commercially available jet plasma system based on Tigres' MEF technology (Tigres GmbH, Marschacht, Germany). The experimental setup is schematically presented in Figure 1.To creates thin active agents-containing layers the plasma system was modified in two ways. The first way contains the extension of the process gas module to evaporate liquid silicon-organic precursor materials suitable for the chemical vapour deposition of silicon oxide films. A Pyrosil® STS 10.0 precursor gas supply (SURA Instruments GmbH, Jena, Germany) was applied to evaporate and feed hexamethyldisiloxane (HMDSO) into the process gas.

The second way is based on the use of a dosing system, build to spray liquids or liquid dispersed particulate materials through a modified plasma nozzle into the active plasma discharge. To form active agent-containing composite films besides the HMDSO main precursor, certain secondary precursors such as metal salt solutions (silver nitrate, copper nitrate, zinc nitrate) were sprayed into the plasma zone, thereby generating the corresponding silver, copper or zinc (oxide) particles in situ, which are embedded uniformly over the whole growing silicon oxide film. The active agent-containing solutions were sprayed directly into the plasma using an in-house made atomizing nozzle and dosing system (EP 2743373B1).

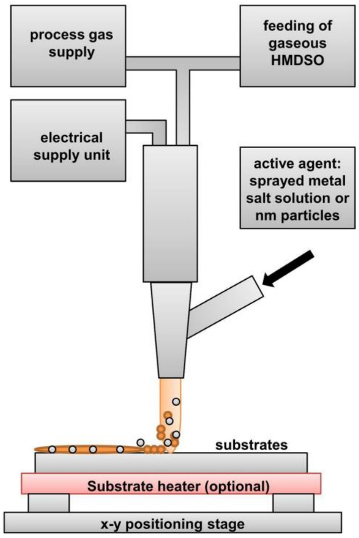

Figure 1: Setup of plasma system used to create silica-like films

Thin film characterisation

X-ray photoelectron spectroscopy (XPS) using an AXID ULTRA DLD (Kratos Analytical Ltd., Manchester, UK) was carried out to determine the chemical composition of the surface. A compensation of charges was achieved in situ and the position of peaks was corrected in reference to the 1s spectroscopic state of carbon (C_{1s}) at 285.0 eV. In XPS investigations a 700 x 300 µm^2 spot was analysed using a 160 eV pass energy (survey) and 40 eV pass energy (detail) and monochromatic Al K_α source. For depth profiling monoatomic mode with 5 keV and 1 mm^2 raster were used. These investigations were performed with a 110 µm aperture using 80 eV pass energy. The sputter depth was measured using an Alpha-Step D600 (KLA Tencor) profilometer.

BacTiter-Glo® (BTG) microbial cell viability assay tests (Promega, Madison, USA) were performed. In these tests, the antibacterial effect of the coating on the non-pathogenic gram-negative bacteria *Escherichia coli* (E. coli) HB 101 was determined. For the test, 10 × 10 mm^2 size samples were immersed in 500 µl of a bacteria suspension (about 2 × 10^6 cells ml^{-1}) in physiological saline [0.9% (w/v)] and incubated for 3 h. Following this, volume parts of 50 µl were transferred in 96 well plates (two replicates) and 50 µl BTG reagent was added to each treated bacteria suspension. Finally, the resulting intensities of luminescence could be measured.

The resistance towards mould was tested based on standard EN 60068-2-10 (2005). In this test, the areal amount of mould growth on top of the coated specimen was determined and compared to untreated specimen. At first, the samples (50 × 50 mm^2) were inoculated with a defined mould spore mixture using the mould strains *Aspergillus niger* DSM 1957, *Paecilomyces variotii* DSM 1961, *Penicillium funiculosum* DSM 1944 and *Trichoderma viride* DSM 1963. The spore concentration was set to 4 × 10^6 spores per ml. Additionally, the mould test was conducted using two approaches. The first approach is a test without a nutrient solution, in the second approach an amount of 3% malt was added to the spore suspension. This malt served as nutrient; as a consequence, this test version represent an intensified examination. Subsequently, the specimens were stored under conditions which accelerate fungal growth (95% air humidity, 26 °C) over a time of 4 weeks. Visual assessment of the mould growth was carried out weekly.

RESULTS AND DISCUSSION

XPS

For these investigation films were deposited on silicon slides. The elemental composition as the function of the sputter depth of a SiO_x layer containing silver, copper and zinc is shown in figure 2. Besides the elements oxygen and silicon, this film contains small amounts of carbon which is randomly distributed. The decrease in the oxygen concentration indicate the film/substrate interface. For a better visibility, the concentration of silver, copper and zinc is multiplied by a factor of 10. All active agents could be found over the whole film cross section. Silver was in cooperated with atomic concentrations between 0.5 – 1.5 at.%. In contrast, elemental concentrations of copper and zinc with values between 0.5 – 3 at.% were higher. Over the sputter depth no quantities of nitrogen could be detected. This argues for a good decomposition of the active agents and nitrate-containing precursors.

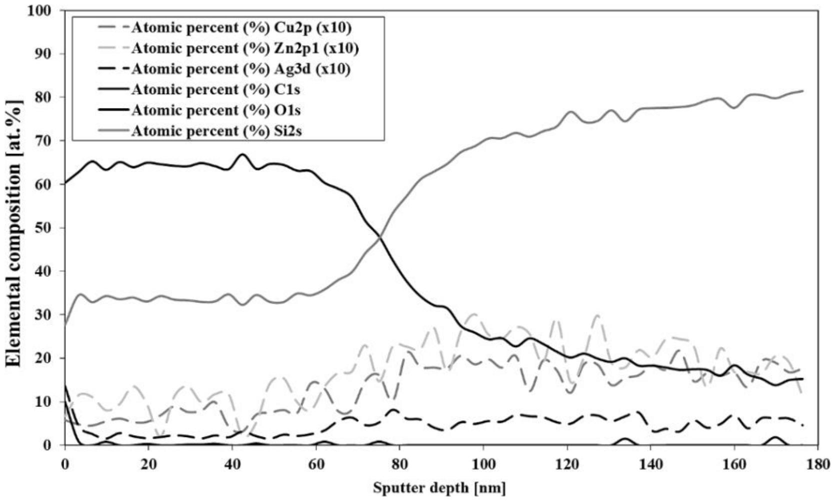

Figure 2: Depth profile (elemental concentration) of silica-like film doped with a combination of the active agents measured by XPS

BTG

The results of the antibacterial BTG test for plasma deposited films on wood are shown in figure 3. The diagrams show the measured luminescence of the treated samples compared to the non-treated wood material (denoted by Wood Ref). Following this approach, the non-treated sample is normalized to 100%. Additionally, the luminescence values of the *E. coli* suspension which were placed in an empty cavity without a specimen (denoted by *E. coli*) are presented in relation to the uncoated wood, too. It is obvious that especially the silver and copper containing films showed the highest bactericidal impact. In the plasma films a decrease of the luminescence to 5% for silver and 1% for copper could be achieved. A reduction to a value of 15% was caused by using zinc-containing precursor resulting in sufficient antibacterial behaviour. The SiO_x-coated but active agent free sample also showed a weak inhibitory effect on this strain resulting in a reduction of the luminescence to 76%. The average value of the unloaded bacteria suspension (*E. coli*) is compared to the untreated wood merely at a luminescence of 29%, which leads to the assumption that the uncoated material serves as area where bacteria can adhere and reproduce faster consequently.

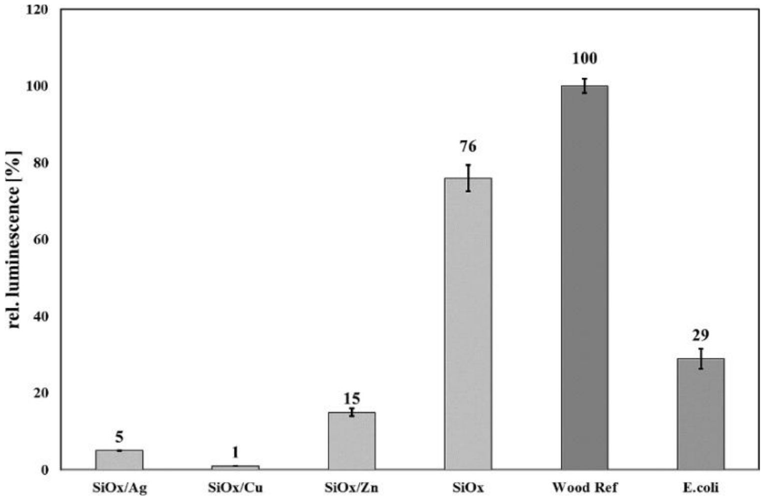

Figure 3: Depth profile (elemental concentration) of silica-like film doped with a combination of the active agents measured by XPS

Mould resistance test

In this investigation, the areal mould growth was assessed on the basis of a rating scale from the standard DIN EN 60068-2-10 and results are shown in table 1 (N normal, I intensified; 0 no mould growth with 50 times magnification; 1 small amount of growth, visible with microscope; 2a spare mould growth, less than 5% of the sample area; 2b mould growth, less than 25% of the sample area; 3 mould growth, more than 25% of the sample area; 3+ strong mould growth, more than 50% of the sample area). The untreated as well as the wood sample coated with an active agent free SiO_x film showed small mould growth after 1 week in the normal test regime. By adding the nutrient to the spore suspension (intensified test regime) a stronger mould growth could be detected on these two specimens. After 2 weeks the mould covered more than 50% of the test area. A similar mould growth could be observed on the samples coated with zinc-containing layers. In the intensified test regime, the silver- and copper-containing layers showed the best inhibition results with lowered mould coverage of less than 5% and 25%, respectively. To improve the antimycotic impact on mould a combination of different active agents implemented in one thin film was prepared and tested. These layers showed a significantly higher activity against mould resulting in no mould growth after 1 week in the normal as well as the intensified test regime. After 2 weeks this sample was not covered with mould in the normal test regime, whereas the intensified test procedure resulted in a slight covering (less than 5%). After 3 weeks, the intensified tested surfaces were covered with more than 25% mould.

Table 12: Results mould resistance test

Sample	**Week I**		**Week II**		**Week III**		**Week IV**	
	N	I	N	I	N	I	N	I
Wood Ref	1	3	3+	3+	3+	3+	3+	3+
SiO_x	1	3	3+	3+	3+	3+	3+	3+
SiOx/Ag	1	2b	3+	3+	3+	3+	3+	3+
SiOx/Cu	1	2a	3+	3+	3+	3+	3+	3+
SiOx/Zn	1	3	3+	3+	3+	3+	3+	3+
SiOx/Ag/Cu/Zn	0	0	0	2a	2b	3	3	3

CONCLUSIONS

By the modification of commercially available plasma jet systems, it was possible to create antimicrobial properties on wood materials in an economical way. Investigations showed that the created films are composed of a silica-like matrix containing small amounts of active agents (Ag, Cu, Zn as well as combinations). A strong antimicrobial impact on bacteria could be shown, especially by using Ag or Cu as active agents. Besides the strong antibacterial effect of thin films containing only one active agent, the antimycotic effect of such films was low towards the mould fungi. To achieve stronger antimycotic properties it was useful to implement combinations of active agents in these films. Further investigations will address the application of these films for the adhesion improvement of commercially available paints and varnishes on wood materials. Also, the resistance of such coating systems (active agent-containing SiO_x + conventional coating) towards microbial colonisation will be investigated in further studies.

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Investigation of Birch Wood Impregnation with Phenol-Formaldehyde (PF) Resins

Juris Grinins[1], Ilze Irbe[1], Vladimirs Biziks[2], Janis Rizikovs[1], Sascha Bicke[2], Holger Militz[2]

[1]Latvian State Institute of Wood Chemistry, 27 Dzerbenes Str., Riga LV-1006, Latvia [email: jurisgrinins@inbox.lv]; [email: ilzeirbe@edi.lv]; [email: j.rizikovs@edi.lv]
[2]Georg August University Goettingen, Institute of Wood Biology and Wood Products, Büsgenweg 4, 37077 Goettingen, Germany [email: vbiziks@gwdg.de]; [email: sbicke@gwdg.de]; [email: hmilitz@gwdg.de]

Keywords: birch, dimensional stability, durability, impregnation, phenol-formaldehyde resin

ABSTRACT

In this study, Silver birch (*Betula pendula spp*.) wood veneers and solid wood blocks were treated with commercial phenol-formaldehyde (PF) resin water solutions. Birch veneers and solid wood blocks of different size were impregnated with PF resin solutions in water with concentrations of 5, 10 and 15 wt%. The weight percent gain (WPG) and bulking after drying and curing of resin treated wood specimens were determined to evaluate the impact of sample sizes and density. The leaching procedure according to EN 84 was performed to evaluate the PF resin fixation stability. The anti-swelling efficiency (ASE) of untreated and treated specimens during seven soaking-drying cycles was examined. Resistance of birch veneers to attack by the brown rot fungus *Coniophora puteana* and the white rot fungus *Trametes versicolor* was assessed according to EN 113.

Higher WPG values were obtained for specimens with lower density, but no correlation was found between the sample size and WPG. The WPG of veneers and solid wood was 5.4–13.0% and 5.5–16.7%, respectively. The ASE of wood blocks treated with PF resins after the 1st cycle was in the range of 29–41% depending on the resin loading in the wood. However, the ASE values decreased after every next soaking-drying cycle, reaching 19–38% after the 7th cycle. After leaching, the WPG of specimens decreased by 1.4–2.1%. All PF treated veneer specimens were very durable (class 1) against decay fungi according to EN 113, while control specimens were slightly or not durable (class 4–5).

INTRODUCTION

Silver birch plywood is widely used in the building industry, construction of transport vehicles, sports gear, furniture, packaging material and toys, but new outdoor applications in high humidity conditions are limited because of the poor biological durability, dimensional and weathering stability. There are great efforts worldwide to develop new wood modification techniques to improve wood material properties. A promising cell wall bulking technique is the use of synthetic resins – N-methylol melamine, phenol-formaldehyde (PF), urea-formaldehyde (UF), melamine-formaldehyde, 1,3-dimethylol-4,5-dihydroxyethyleneurea (DMDHEU) etc. Treating wood with water-soluble resins is a known and effective method to improve the dimensional stability and expand the durability of wood. Stamm and Seborg (1939) have tested different resin forming materials: PF, UF, and methacrylate intermediates, of which they selected PF-based resins as being the most promising for treating veneers for plywood manufacture. The use of PF as an impregnate is a long-known method to protect plywood against wetting and to improve surface hardness, dimensional and weathering stability (Stamm and Seborg 1941). PF treatment is an alternative to conventional preservation of wood and enhances the resistance to biological decay agents without using biocidal compounds. PF resins are able to penetrate into various morphological regions of wood tissues and into the cell wall by diffusion. After curing, the fixation of the resin is provided by the formation of a rigid three-dimensional network in the wood structure (Kielmann *et. al.* 2013) Dimensional stabilization due to PF modification is attributed to cell wall bulking. Bulking reduces the pore size in the cell wall matrix so that less space can be occupied by the water molecules. This results in reduced cell wall moisture content, limited access to the cell wall interior by decay agents, and, as a consequence, in high resistance to decay fungi (Furuno *et. al.* 2004). The aim of our study is to obtain plywood made of PF resin treated veneers with improved dimensional stability and biological durability.

EXPERIMENTAL

Materials

Different specimens from air-dried boards of Silver birch wood (20x20x5, 25x25x10 and 20x20x20 mm^3, *L*×*R*×*T*) were prepared for impregnation tests. Oven-dried weights were determined after drying at 103±2°C for 24 h. Birch veneer specimens (100x100x1.5 mm^3) were cut from ten different veneer sheets. Ten wood blocks and veneers were used per treatment. 35 specimens with the size of 20x20x5 mm^3 were used per treatment.

Phenol-formaldehyde resins

Before being used for impregnation, the stock solution of the PF resins was diluted with distilled water to 5%, 10% and 15% (w/w). Different characteristic parameters of resins are listed in Table 1.

Table 1. Characteristic parameters of PF resins used in the study

Viscosity [mPas]	Solid content [%]	Molecular weight Mw	Molecular weight Mn	Density [g/cm^3]	Free formaldehyde [%]	Free phenol [%]
259	55.7	705	460	1.195	<0.8	<2.5

Treatment of wood

Oven-dried specimens were impregnated with solutions of PF resin in a laboratory glass reactor via a two-step impregnation method. The vacuum step (time – 1h, pressure 2 kPa) was used to ensure the air ejection from the specimens. To ensure the diffusion of the PF oligomers into the wood cell walls, the specimens were submersed (time – 2h, pressure 101.32 kPa) in the solutions (the second step). After impregnation, the specimens were oven dried, and the weight percent gain (WPG) was calculated to assess the amount of PF resin in the wood. To avoid crack formation during drying, the temperature was gradually increased. The resin was cured at 140°C for 1 h. The average WPG was calculated for each treatment according to (Eqn. 1.),

$$\text{WPG (\%)} = ((M_1 - M_2)/M_1) \times 100 \qquad (1)$$

where M_1 is the oven-dried mass of the modified specimens and M_2 is the oven dry mass of the unmodified specimens.

Leaching

Leaching was performed over 14 days according to EN 84 – Accelerated aging of treated wood to verify the chemical fixation of PF in the wood. After 14 days, the excess water was blotted off, and the specimens (20x20x5 mm^3) were dried in an oven with stepwise temperature increase. The dry weight after the test was determined, and the amount of leached PF resin was calculated.

Anti-swelling efficiency (ASE)

The ASE of 10 conditioned specimens with dimensions of 20x20x20 mm^3 was examined under cyclic conditions according to DIN 52184 (1979). Seven full cell-saturation cycles with water and oven drying were carried out. The average of the thickness, width, and length swelling measurements formed the basis for the ASE calculation.

Decay test

The resistance of PF treated birch veneers to attack by wood destroying fungi was assessed according to the modified European Standard EN 113 (1996). Impregnated and control specimens (50x25x1.5 mm^3) were exposed to the brown rot fungus *Coniophora puteana* BAM Ebw 15 and the white rot fungus *Trametes versicolor* (L.) Lloyd (CTB 863A) in Petri dishes on a medium containing 5% malt extract concentrate and 3% Fluka agar (Sigma-Aldrich). Sterilised specimens were aseptically placed on steel supports and incubated at 22±2°C and 70% RH for 6 weeks. Subsequent to cultivation, the specimens were removed from the culture vessels, brushed free of mycelium and oven dried at 103±2°C. The loss in dry mass (%) of the specimens was used as the criterion for determining the extent of the fungal attack.

RESULTS AND DISCUSSION

Weight percent gain (WPG) and bulking

The degree of treatment was assessed directly as the WPG of the PF resin treated wood. Figure 1 shows the average WPG of birch wood blocks and veneers after impregnation and curing at three different solution concentrations (5, 10 and 15%).

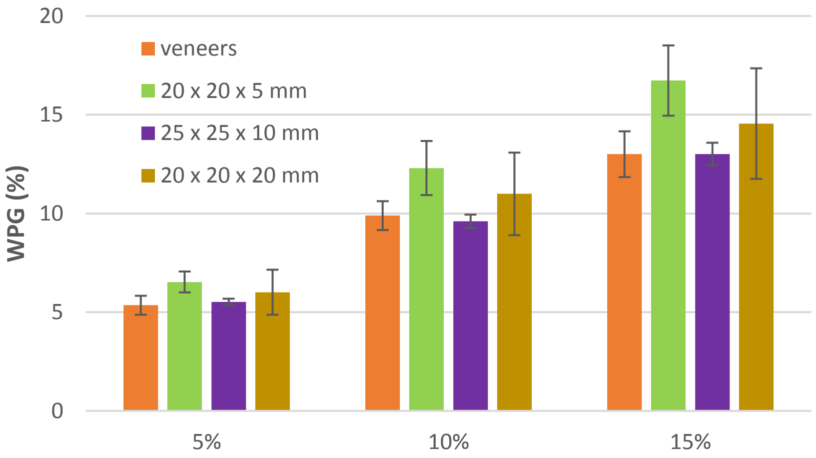

Figure 1: Weight percent gain (WPG) of different size PF resin treated birch wood blocks and veneers

The WPG increased linearly with increasing concentration of the PF resin solutions, and it seems that the tested resin was able to penetrate into the wood blocks and veneers. The highest WPG (6.5–16.7%) was found for 20x20x5 mm^3 specimens, but there was no correlation between the sample size and WPG. Veneers and 25x25x10 and 20x20x20 mm^3 block specimens had similar WPG at all tested solution concentrations.

WPG values are insufficient to determine whether the resin has infiltrated into the cell walls or only the wood cavities and therefore also bulking was determined. Bulking increased at higher concentrations of the PF resin solution (Table 2). The largest impregnated wood specimens (20x20x20 mm^3) had a lower bulking effect compared to the case of 25x25x10 mm^3 at all tested

PF resin concentrations. Most likely, the penetration of PF resins in deeper layers was limited in the thicker sample.

Table 2. Bulking of PF resin treated birch wood blocks of different size

	Bulking (%)	
Treatment	**25 x 25 x 10 mm^3**	**20 x 20 x 20 mm^3**
5%	4.2±1.2	2.2±0.5
10%	5.7±1.1	4.3±0.8
15%	6.6±1.3	5.2±1.1

To verify the chemical fixation of PF resin in the wood, leaching according to EN 84 was performed (Table 3). The WPG of the PF treated specimens after leaching decreased by 1.4–2.1% at all concentrations. The total loss of the WPG of specimens was 10.1–20.4%. Leaching can be attributed to the loss of resin from the surface, but the weak fixation could be explained by the insufficient network within the cell wall. However, resins were comparatively well fixed in wood blocks even after the leaching test.

Table 3. Weight percent gain (WPG) of PF resin treated birch wood before and after leaching according to EN 84

	WPG (%)		
Treatment	**before**	**after**	***ΔWPG* (%)**
5%	6.6±0.5	5.2±0.4	-20.4
10%	12.8±1.4	10.7±1.3	-16.4
15%	17.1±1.6	15.4±1.6	-10.1

Anti-swelling efficiency (ASE)

Traditionally, modified wood is used in outdoor conditions. In such an application, the dimensional stability is essential under cyclic conditions. Therefore, the PF treated birch wood was passed through several wetting and drying cycles (Figure 2). The ASE values of the PF resin treated wood after the 1st soaking-drying cycle were 29%, 33% and 41% at the solution concentration of 5–15%, respectively. During the test, ASE tended to decrease. Compared to the 1st cycle, the ASE of the PF treated birch specimens after 7 cycles decreased by 36%, 11% and 8% at the solution concentrations of 5, 10 and 15%, respectively. In terms of ASE, treatment with 10 and 15% solutions seems to be reasonable to ensure long term dimensional stability.

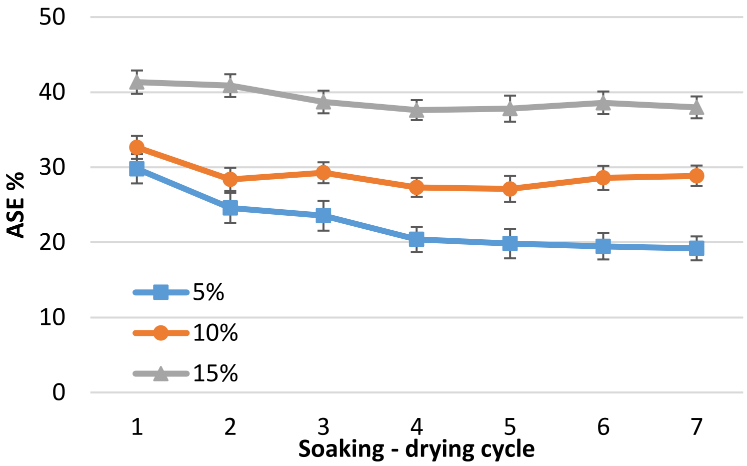

Figure 2: Anti-swelling efficiency (ASE) of PF resin treated birch wood

The cell wall total water capacity (CWTWC) of untreated birch wood (33%) was higher compared to that of the PF treated specimens (17–24%) (Figure 3). CWTWC is lower with higher resin loading in the wood. During 7 soaking-drying cycles, CWTWC is increasing, and it can be explained by the leaching of natural extractives in the case of untreated wood and the PF resin leaching from the treated wood (Table 3). Probably, a part of the PF resin penetrated into the cell wall is weakly fixed during the curing process and therefore is leached out during soaking-drying cycles, leading to increased water capacity.

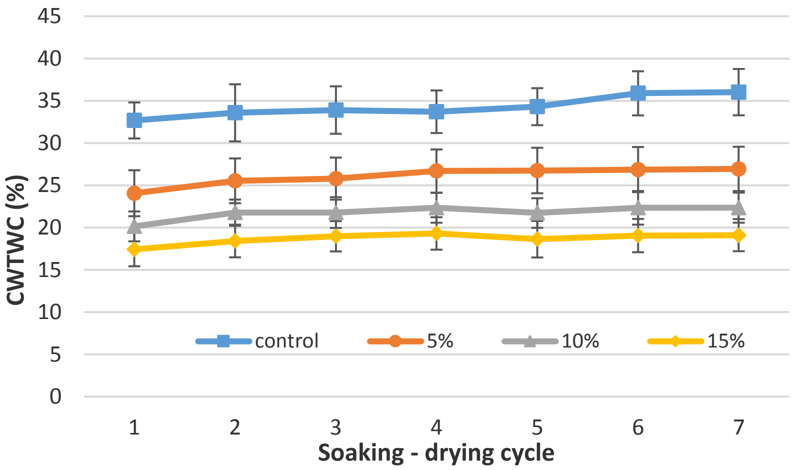

Figure 3: Cell wall total water capacity (CWTWC) of PF resin treated birch wood

Decay resistance

An essential aspect is the better biological durability of PF treated wood. The results of the test EN 113 show that the lowest decay resistance against both tested fungi was for veneer control specimens, while all PF treated veneer ML did not exceed 1% (Table 4). According to CEN/TS 15083-1, veneer control specimens are slightly or not durable (durability class 4 and 5), depending on the fungus, while all PF treated specimens are very durable (durability class 1). Absolute moisture values after the decay test testify that the moisture during the test was sufficient for fungal growth. After the leaching according to EN 84 (data not shown), the ML of 5% PF treated birch wood blocks did not exceed 10%, resulting in durability class 2–3, while the 10 and 15% PF treated specimens were very durable (class 1). This suggests that using a 10% concentration of PF resin is sufficient for fungal resistance.

Table 4. Mass loss (ML) and absolute moisture content (W_{abs}) of PF treated veneer specimens after attack by the brown rot (Coniophora puteana) and white rot (Trametes versicolor) fungi

	Coniophora puteana		***Trametes versicolor***		***Durability class CEN/TS 15083-1***
Treatment	**ML**	**W_{abs}**	***ML***	**W_{abs}**	
Control	36.8±3.8	41.0±15.5	25.6±4.0	45.4±4.1	4-5
5%	0.7±0.2	29.9±6.0	0.9±0.2	46.2±4.7	1
10%	0.1±0.1	42.8±6.4	0.4±0.3	27.6±5.1	1
15%	0.0	38.8±13.5	0.0	51.8±14.6	1

CONCLUSIONS

The WPG of birch wood increased linearly with increasing concentration of the PF resin solutions. Higher WPG values were obtained for specimens with lower density, but no correlation was found between the sample size and WPG. After leaching, the WPG of PF treated specimens decreased at all PF concentrations, but resins were comparatively well fixed in wood blocks. The dimensional stability of PF treated birch wood was improved significantly. The ASE of the treated wood was 19–38% at the end of testing. The treatment of birch wood with PF resins has a strong positive effect on the resistance of birch veneers to basidiomycete decay. Without leaching, all PF treated veneers were very durable against brown and white rot fungi. After leaching tests, 10% and 15% PF resin treatments were sufficient for very durable material. Our results suggest that the 10% PF resin treatment is suitable for the improved dimensional stability and biological durability of birch wood.

ACKNOWLEDGEMENTS

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Thermal properties and density profile of poplar wood (*Populus nigra* L.) thermally and thermo-mechanically modified

Marek Grześkiewicz[1] and Karol Poddębski[1]

[1]Faculty of Wood Technology, Warsaw University of Life Sciences - SGGW,
Nowoursynowska 159, PL 02-78 Warsaw, [email: marek_grzeskiewicz@sggw.pl]

Keywords: density profiles of wood, poplar wood, thermal modification, thermal properties of wood, thermo-mechanical densification

ABSTRACT

This paper presents a part of research regarding testing mechanical and physical properties of poplar wood (*Populus nigra* L.) after modifications to improve its selected properties. Thermal modification and thermo-mechanically densification methods were used. At the beginning, wood was thermally modified in the atmosphere of superheated steam in two temperatures, everything (in industrial conditions). At the end of the process of wood thermal modification, wood was moistened to EMC of normal climate. After the process of thermal modification wood was thermo-mechanically densified in industrial conditions using high pressure press and cyclic pressing. Parameters of wood densification were different for natural wood and thermally modified wood to obtain acceptable level of wood destruction in outer zone. This parameters were determined in laboratory conditions using testing machine, heated plates and small wood samples. The tests of wood were conducted in order to examine the influence of thermal modification and thermo-mechanical densification processes on the density, density profiles and selected thermal properties of poplar wood. The analysis of the research results led to the recognition of significant changes in wood properties. Natural poplar wood was successfully densified from 435 kg/m^3 to 700 kg/m^3 without any cracks. Thermal modification reduces wood's density and thus makes it problematic to densify thermally modified to the same thickness or density as not modified one. Poplar wood thermally modified in 183 °C was densified to 558 kg/m^3 while that modified in temperature 193 °C was densified only to 450 kg/m^3. Density profiles of compressed wood, determined using GreCon density profilometer, show lower homogenous structure of new material compared to control wood. Thermal properties of tested wood: thermal conductivity, volume heat capacity and thermal diffusity were determined with portable system for measurement of heat transfer properties ISOMET 2114, Applied Precision (type measurement probe IPS 1100). The process of thermal modification improved insulating qualities of the tested wood lowered the thermal conductivity and decreased its density. Thermo-mechanical densification of the tested wood led to an increase in both density and thermal conductivity along with its volume heat capacity (VHC).

INTRODUCTION

There are many articles regarding testing properties of thermo-mechanically poplar wood modification, solid wood and veneers. For example MOE of viscoelastic thermal compressed (VTC) solid poplar wood was determined by Kamke 2006, properties in relation with water by Sözbir 2017. The effect of thermo-hydro-mechanical (THM) densification temperature on the surface of hybrid poplar, roughness, wettability and chemical composition was tested by Diouf *et al.* 2011. Densification of wood veneers by compression combined with heat and steam and selected physical and mechanical properties of modified veneers were determined by Fang *et* *al.* 2011. For poplar boards 25 mm thickness tests were made by Candan *et al.* 2013. Song *et al.* 2018 tested mechanical and physical properties of densified poplar wood and other species after chemical treatment to reduce lignin and hemicellulose content. They compare some properties to materials other than wood

EXPERIMENTS

Dry sawn timber made of poplar wood, of the dimensions 130x30x2500mm and 130x40x2500 mm was used for tests. Elements were cross cut into three parts. One of them was control (not modified) and next two were thermally modified in two different temperatures. Thermal modification was carried out in industrial small chamber for thermal modification (Hamech, model PW-10), of capacity about 5 cubic meters (Figure 1). Applied temperatures were 183 °C and 193 °C and time (270 min) was the same for each temperature. At the beginning of the process hot air was used. Then, in temperature of about 130 °C, superheated steam was introduced into the chamber, so primary process was carried out in this atmosphere. At the end of the process the wood was cooled down to the temperature of about 50^0C and then moistened with wet steam to equilibrium moisture content equivalent to long lasting seasoning in normal climate conditions. After process of TM in temperature183 °C and 193 °C the wood had different humidity - 5 and 4% respectively. Half of sawn timber elements from control and from wood thermally modified earlier in two mentioned temperatures, were next modified using high pressure press (Italpresse, model GL/260-PS) (Figure 2). In this part of the experiment wood was heated between central parts of press shelfs (dimension 0,5x2,5m) to obtain the same temperature of about 90 °C in the whole volume of modified elements. Then the wood was pressed in three steps, at the end of wood pressing significant spring back was observed. Parameters for wood densification were determined experimentally for small wood samples (50x50x30 mm, 50x50x40 mm) using heated units between plates of testing machine Instron (Figure 3).

Density and thermal properties of poplar wood modified and controlled was determined for wood seasoned in normal climate conditions.

Figure 1: Chamber for thermal modification of wood, Hamech (model PW-10)

Figure 2: Press for wood densification, Italpress (model GL/260-PS)

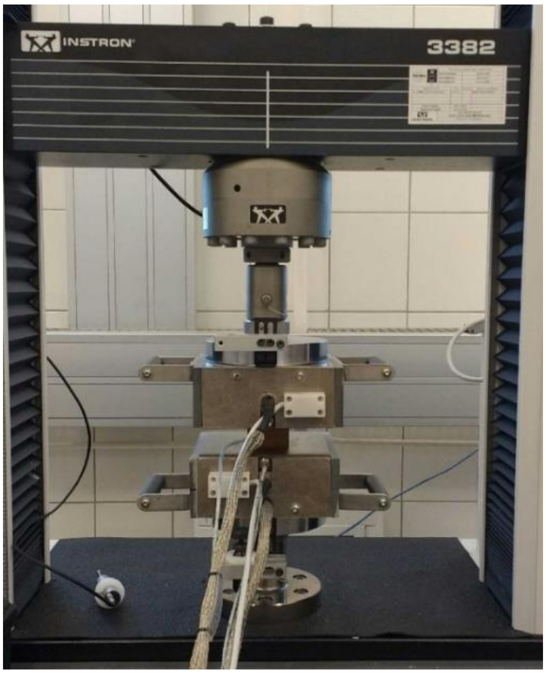

Figure 3: Set of heated units used in laboratory condition for the determination of wood densification parameters

RESULTS AND DISCUSSION

Average density of wood samples and their thickness, before and after densification are presented in Table 1, for n=3 (samples chosen only for thermal properties determination) and for n=20 (all samples used for density determination). For natural poplar wood density increase ratio is 1,61 while for thermally modified wood in temperature 183 °C and 193 °C it is 1,41 and 1,32 respectively. It was impossible to densify thermally modified wood to higher density with acceptable level of cracks in outer zone of densified samples. Wood thermally modified in higher temperatures is characterized by susceptibility to crumbling.

Some samples cross section scans, before and after densification, are presented on Figure 4, while their density profiles are presented on Figure 5, 6 and 7. As a result of wood densification less homogenous density profiles were obtained compare to natural wood and thermally modified wood. Density profiles were determined for 50x50 mm samples.

Table 1: Average density of control natural poplar wood and modified wood (n=3, samples used for heat properties determination, n=20 samples used for density determination

Type of wood modification	**Thickness [mm]**	**Density [kg/m^3] n=3 / n=20**
Control, natural wood	29,18	436/435
Densified thermo-mechanically natural wood	19,25	624/700
Thermally modified wood in 183 °C	30,29	335/395
Densified thermo-mechanically thermally modified in 183 °C	22,30	473/558
Thermally modified wood in 193 °C	29,95	324/342
Densified thermo-mechanically thermally modified in 193 °C	22,81	455/450

<table>
<tr><td>Natural before densification</td><td>Densified natural wood</td></tr>
<tr><td>Thickness 29,49 mm, density 405 kg/m^3</td><td>Thickness 18,23 mm, density 714 kg/m^3</td></tr>
<tr><td colspan="2"></td></tr>
<tr><td>Thermally modified in 193 °C</td><td>Densified thermally modified in 193 °C</td></tr>
<tr><td>Thickness 20,18 mm, density 331 kg/m^3</td><td>Thickness 22,4 mm, density 440 kg/m^3</td></tr>
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Figure 3: Poplar wood samples - scan of cross section before and after densification

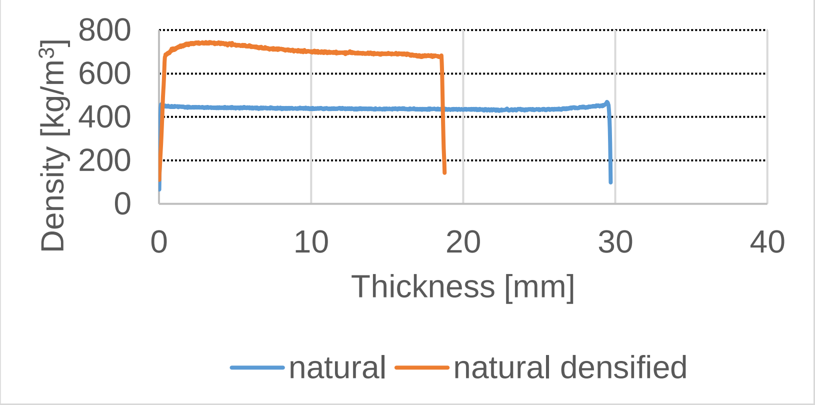

Figure 4: Density profile of selected sample of control (natural) poplar wood and thermo-mechanical and densified wood

Thermal properties of modified wood are presented in Table 2. The process of thermal modification improved insulating qualities of the tested wood (lowered the thermal conductivity) and decreased its density. Thermo-mechanical densification of the tested wood has led to an increase in both density and thermal conductivity along with its volume heat capacity (VHC).

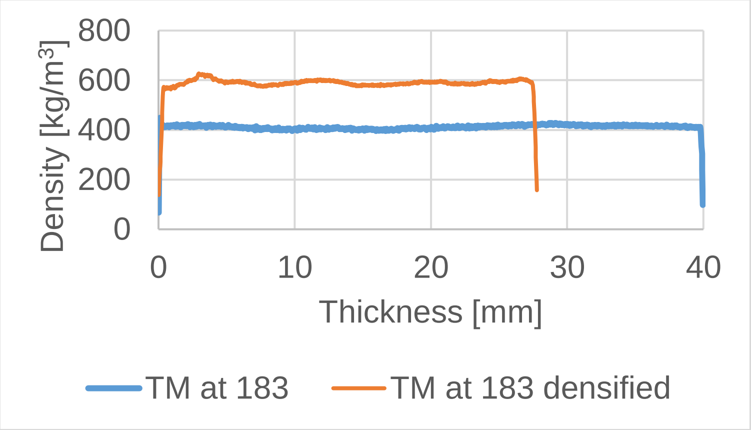

Figure 5: Density profile of selected sample of thermally modified (TM) poplar wood in temperature 183 °C, 270 min, before and after densification.

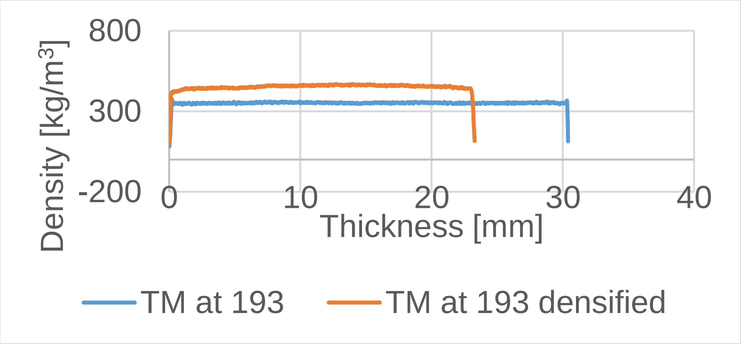

Figure 6: Density profile of selected sample of thermally modified (TM) poplar wood in temperature 193 °C, 270 min, before and after densification

Table 2: Thermal properties of control poplar wood and modified wood

Type of wood modification	**Thermal properties**		
	Thermal conductivity [Wm^{-1}K^{-1}]	**Volume heat capacity [Jm^{-3}K^{-1}x10^{6}]**	**Thermal diffusity [m^{2}s^{-1}x10^{-6}]**
Control, natural wood	0,1289	0,5215	0,2475
Densified thermo-mechanically natural wood	0,1489	0,6641	0,2241
Thermally modified wood in 183 °C	0,1044	0,4324	0,2446
Densified thermo-mechanically thermally modified in 183 °C	0,1269	0,5180	0,2456
Thermally modified wood in 193 °C	0,0951	0,3500	0,2721
Densified thermo-mechanically thermally modified in 193 °C	0,1262	0,3969	0,2321

CONCLUSIONS

Thermal modification of poplar wood reduces its density. Density for TM wood in 183 °C and 193 °C is 8,7% and 21,4% respectively and is lower compare to the control natural wood.

Densified natural poplar wood had higher thermal conductivity than control natural wood (0.1489 W/mK). The lowest thermal conductivity was obtained for thermally modified wood. in the case of thermally modified wood in temperature 193 °C reduction was 26% comparing to the control wood.

The higher volume heat capacity was observed for densified natural poplar wood 0.6641 J/Km^3[x10^6]. Wood densification increases values of volume heat capacity by 27% compare to the control wood.

The highest thermal diffusity was in the case of poplar wood thermally modified in 193 °C (0.2721 m^2/s [x10^{-6}]).

Wood thermo-mechanically densified is characterised by lower homogeneity density profiles compare to the natural wood and thermally modified wood.

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Water sorption properties of surface charred wood

Maija Kymäläinen[1], Saara Hautamäki[2] and Lauri Rautkari[3]

[1]Aalto University, Dept. of Bioproducts and Biosystems, P.O. Box 16300, FI-00076 Aalto [email: maija.kymalainen@aalto.fi]

[2]Aalto University, Dept. of Bioproducts and Biosystems [email: saara.hautamaki@aalto.fi]

[3]Aalto University, Dept. of Bioproducts and Biosystems [email: lauri.rautkari@aalto.fi]

Keywords: Sorption; Surface modification; Thermal modification; Wood; Wood char

ABSTRACT

Spruce wood samples were subjected to a one-sided surface modification process using a hot plate at temperatures of 250 and 400 °C. The effect of time was studied in both temperature settings. The charring was executed on the pith side of the samples. The sample was either compressed or merely held in place by a small weight. The water sorption properties of the modified surface were investigated with contact angle measurements, as well as a water floating experiment. Both the compressed and uncompressed samples showed improved hydrophobicity compared to unmodified reference. The samples treated at 250 °C showed highest contact angles. In general, surface compression seemed to reduce wettability measured by floating more, and the differences between treatment temperature-time combinations were smaller than for the uncompressed samples. The samples charred at 400 °C performed better when surface compressed, which could be related to a more closed surface structure.

INTRODUCTION

Modification processes, such as thermal modification, aim to increase the durability and service life of wood in demanding conditions. However, different modifications do not entirely prevent weathering of the cladding boards, and cupping, erosion and checking may take place (Jämsä *et al.* 2000). Additionally, fading of colour is also not always a desired feature. The exterior structures demand maintenance at even intervals, which forms a substantial part of the life cycle costs of a building (Grüll *et al.* 2011). The modification processes also extend all through the material, when modifying only the exposed surface would often suffice. Some processes are very time consuming and significantly increase the price of the product.

One-sided surface charring of wood could be a durable alternative to increase the service life of wooden claddings. The process is simple and relatively fast. Charring is a traditional Japanese technique (*shou sugi ban*) used to increase the durability and service life of cladding boards. In this technique, wood is burned from the surface with naked flame or a heated iron pad, and the appearance is said to last for decades. The surface can be brushed and oiled, and the colour does not fade. The commercial techniques available nowadays often use a gas flame to modify the surface. While it is possible to regulate the appearance with this type of technique, it is not possible to control the temperature and extent of charring. The result is bound to be inconsistent, as the surface is left uneven with areas of thicker and thinner char layer, and cracking is hard to avoid. Char is also a porous substance and readily absorbs available capillary water.

Using a hot plate with a weight to keep the wood piece flat facilitates regulation of temperature, and produces an evenly charred surface. The temperature can be accurately controlled, and the produced surface is harder and not as flaky as the surface created by flame charring. This reduces the surface porosity and improves the water sorption properties. Applying simultaneous densification leaves the surface even harder and is hypothesized to further improve the hydrophobicity.

Using wood in buildings has a long history in Finland, and the interest is increasing. Wood is an easy, ecological and economical material that, with proper treatment, will also be durable and long-lived even in demanding outside conditions. The most popular material for claddings and sidings is spruce (*Picea abies* L.). The heartwood is often facing outside as it cracks less than the sapwood side. This in mind, spruce samples were charred on the pith side and their water sorption properties evaluated by contact angle and water floating measurements to evaluate the hydrophobicity of the charred surface in relation to unmodified reference samples.

EXPERIMENTAL

The spruce sapwood samples were sawn to dimensions of 90 x 90 x 15 mm (tangential x longitudinal x radial), or to 100 x 50 x 20 mm. Two sizes were used because the hot plate used was changed in between the measurements, but this was judged not to affect the surface properties. The samples were charred on the pith side with a hot plate using different time-temperature combinations, 20–50 samples per combination. The longer holding time (30, 60, 120 min) was examined with a low temperature of 250 °C, and the shorter (30 s, 3 min) with a high temperature of 400 °C. A weight or a moderate surface pressure was used to avoid cupping during the modifying process. The weight resulted in a surface pressure of 0.07–0.11 N/mm^2, while the densification pressure exerted by a laboratory hydraulic press was 10.0 N/mm^2 (Weverk ab, Karlstad, Sweden). Thermal conductance was measured without simultaneous compression by using thermocouples and a logger (Eltek Series 1000 Squirrel Meter/Logger). The wettability was assessed by contact angle measurements by using a drop size of 8.7 µl and measurement period of 1000 ms (10 samples per treatment, 3 measurement points, sessile drop) (Cam 2000, KSV Instruments Ltd, Finland), as well as water floating for a period of 0 to 72 h (10 samples). The floating samples were sealed from the sides by a polyurethane-based jointing material prior to experiment.

RESULTS AND DISCUSSION

The thermal conductance measurements revealed that the applied heat affects only the very surface of the wood (Figure 1). After the first millimetre, the temperature decreases fast. The limit for charcoal formation is commonly thought to lie between 288 and 300 °C (Schaffer 1967, Babrauskas 2005), and naturally only the higher temperature of 400 °C resulted in formation of an actual char layer. This would leave the chemical composition of the samples somewhat different, as at 250 °C the reactions are mainly endothermic and temperatures above 280 °C are characterised by exothermicity. Up to 250 °C, cellulose degrades to water, CO_2 and CO, but at this temperature some hemicelluloses and glucose are still available and some OH-groups still intact (Antal 1982, Pastorova *et al.* 1994, Antal and Grønli 2003). The short exposure to 400 °C resulted in a slightly thinner char layer, and most likely also a thinner pyrolysis layer beneath the char. The pyrolysis layer is all but missing in the samples modified at 400 °C for 30 seconds, as the temperature reached only facilitates some water evaporation (Figure 1b). The pyrolysis layer (about 1 mm beneath the surface) is similar to thermally modified wood, except that it has most likely experienced more extensive oxidation reactions compared to procedures that employ shielding gases such as steam. However, the process duration is less than that of a thermal modification process. On the other hand, temperature is a more important variable than holding time when considering the product composition (Antal and Grønli 2003). The pyrolysis layer is speculated to have an effect on the long-term weathering characteristics of charred wood, if the surface layer is damaged, but is likely to have a small effect on the short-term experiments presented here.

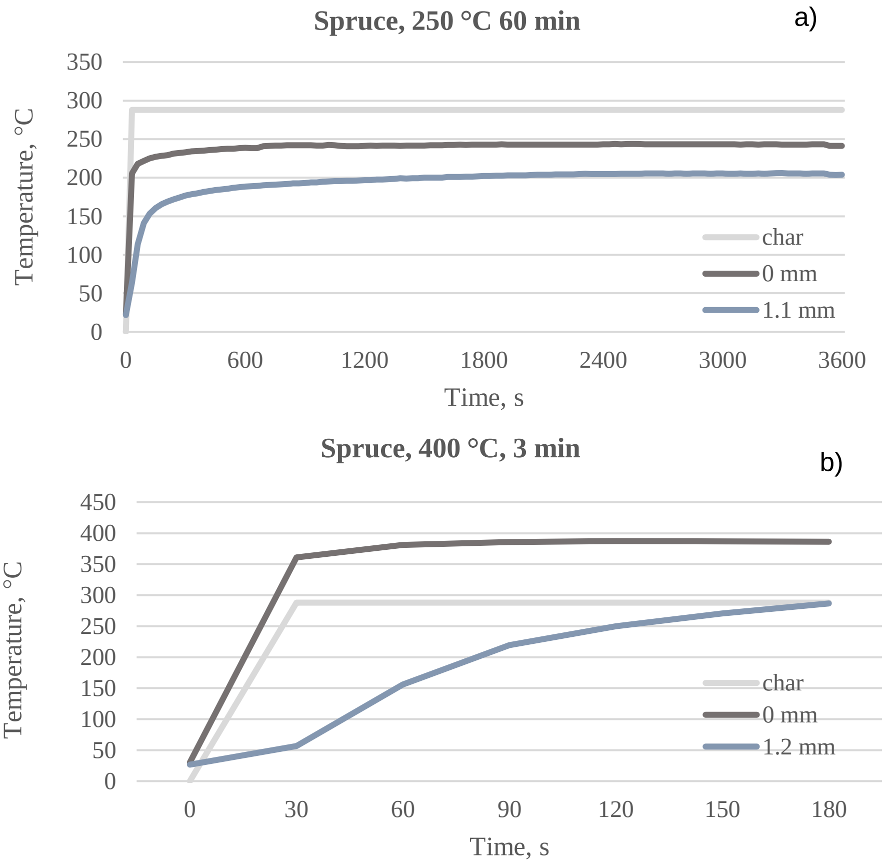

Figure 1. Thermal conductance of spruce charred at 250 ℃ (a), and 400 ℃ (b). The "char" line depicts the base of the char front at 288 ℃.

Charring had an overall positive effect on the wood contact angles. The surface densification unexpectedly slightly lowered the contact angles compared to uncompressed wood samples, as higher hydrophobicity was expected because of a harder surface. However, the contact angles of the densified samples were closer together and showed less change in time compared to uncompressed samples (Figure 2). Highest contact angles were obtained with samples treated at 250 °C for 30–60 minutes for both uncompressed and compressed samples. Thus, the less altered chemical composition of samples treated at 250 °C does not affect the wettability negatively, but these samples in fact perform better than the more severely charred samples. Exposure to high temperature will crack the wood surface as the thermally induced reactions and vaporisation of wood components will be more violent than at lower temperatures. This will leave the surface more porous and therefore more susceptible to wetting than the surface of samples at lower temperatures. The severely modified samples (400 °C) showed lowest contact angles, from which the uncompressed samples exhibited a quite drastic decline in the angle in relation to time. This could be related to the applied surface pressure closing some of the porosity, and also flattening the surface by plasticizing the fibres, therefore reducing the available surface area. The longer time (30 seconds vs. 3 minutes) can have some effect, but this is thought to be minor, as the limit of 288 °C was exceeded on the surface in both cases.

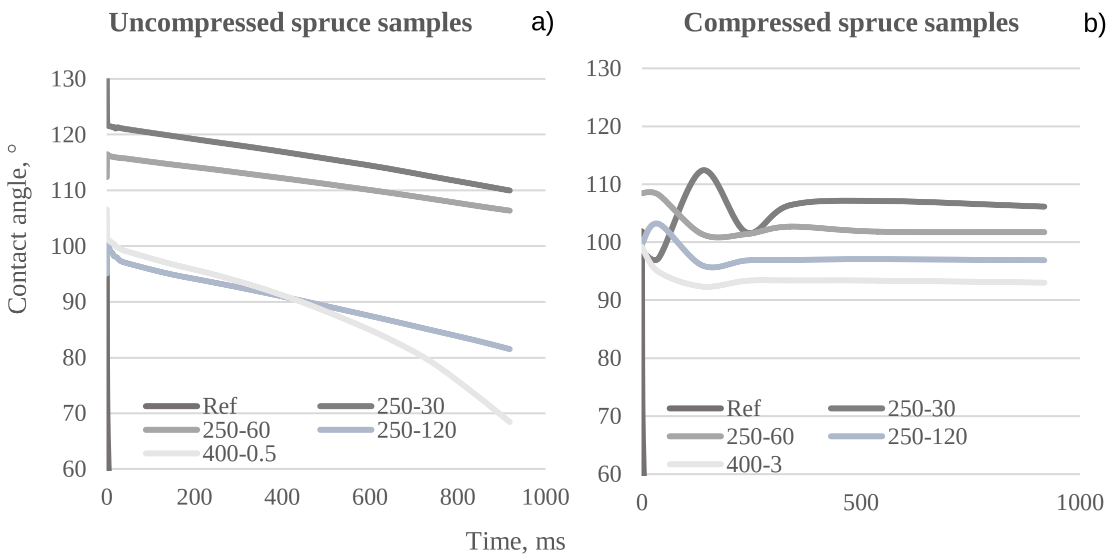

Figure 2: Contact angles for uncompressed (a) and compressed (b) spruce sapwood samples. The code depicts temperature in °C and time in minutes (e.g., 250 °C, 30 min)

The water floating experiment results are shown from all samples (Figure 3) except for surface compressed spruce at 250 °C for 120 min, because of inadequately sealed sides that cause complete wetting of the samples. For the uncompressed samples, the absorption measured by floating reduced from reference to the sample modified at 250 °C for 60 min, but increased again with longer treatment time as well as more severe temperature. The surface compressed samples showed low absorption with shorter holding time (30 min, 3 min) and the overall moisture contents remained lower for the 72 h period compared to uncompressed samples. Here, as well as in the contact angle measurements, it is difficult to make direct comparisons on which temperature is the best performing.

Both the sorption tests indicate that a prolonged period of exposure and/or a higher temperature affect the hydrophobicity negatively, although simultaneous densification seems to offset some effects. This is likely related to the surface cracking, which provides water passages to the unmodified wood beneath the char and pyrolysis layers. Fast one-sided charring could be a feasible method to modify spruce wood to gain a durable, hydrophobic surface. The results indicated that a simultaneous surface densification could improve the surface sorption properties at least in short term. However, it is difficult to say whether a high temperature for a short time or a low temperature for a long time would be a better option. The unmodified wood remaining beneath the char and pyrolysis layers is also susceptible to some moisture adsorption, and therefore dimensional changes cannot be ruled out. This may affect the durability of the surface in the long run.

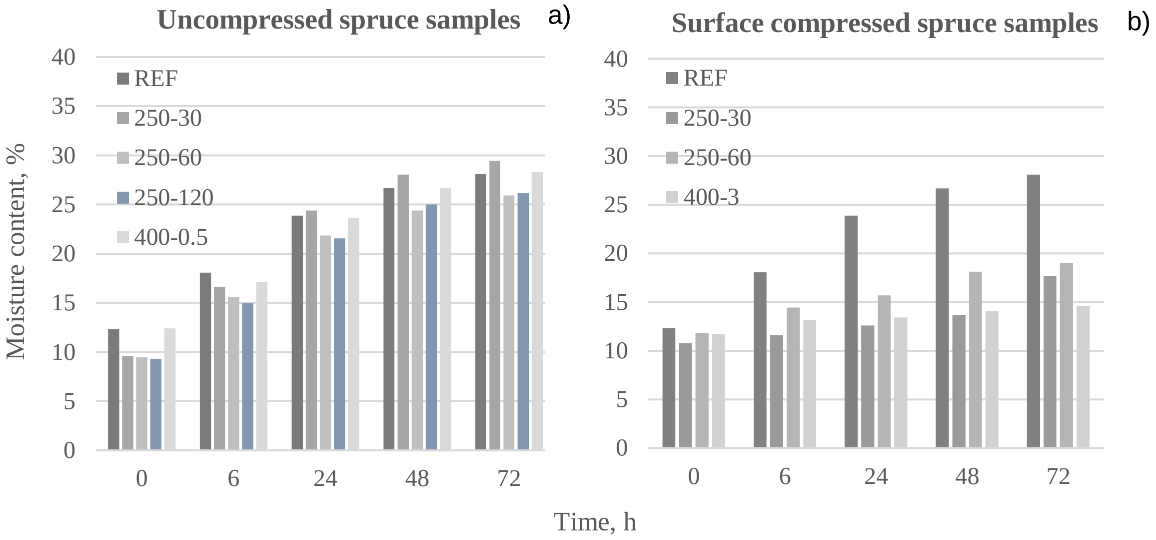

Figure 3. Water floating results of uncompressed (a) and compressed samples (b).

CONCLUSIONS

One-sided surface modification by charring was implemented for spruce samples. The effect of temperature, time and surface pressure was investigated in terms of water sorption properties. Simultaneous densification levelled the differences between treatments and reduced the effect of time in both sorption tests. This could indicate the creation of a surface that has higher resistance to moisture and some moisture-induced changes. Densification may also restrict cracking to some extent. With longer holding time, the wood is affected deeper, creating a wider transition zone from charred surface to inner virgin wood. The effect of this thermally modified layer needs to be investigated in terms of its protective potential when wood cracks during long-term weathering.

ACKNOWLEDGEMENTS

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Energy dispersive x-ray fluorescence (ED-XRF) for the multi-elemental analysis of thermally modified wood treated with coatings systems

René Herrera Díaz[1], Marco Fellin[2], Martino Negri[3], Jalel Labidi[4]

[1] University of the Basque Country, Spain [renelaexander.herrera@ehu.eus]

[2] CNR-IVALSA, Trees and Timber Institute, TN, Italy [marco.fellin@muse.itl]

[3] CNR-IVALSA, Trees and Timber Institute, TN, Italy [negri@ivalsa.cnr.it]

[4] University of the Basque Country, Spain [jalel.labidi@ehu.eus]

Keywords: wood recycling, pullulans, TMW, coating systems

ABSTRACT

Thermally modified wood (TMW) is currently used in Europe in many indoor and outdoor applications, principally due to the improved intrinsic properties and to environmental benefits. Despite its enhanced durability, a surface treatment is usually required in TMW products in order to avoid discolorations and surface degradations during service life. The use of coating systems becomes necessary and the commercially available products need to be tested on the modified surfaces taking in to account among others, the pullulans transfer to the atmosphere or soil, the performance during service life and at its end of life. In this study, Ash wood samples thermally treated at 192, 202 and 212 ºC were finished with wood coating systems and then artificially weathered (80 cycles, 2120 hours). Afterwards, the elemental concentration of unmodified and modified wood, coated samples and weathered samples, were measured by using Energy Dispersive X-ray Fluorescence (ED-XRF) analyzer. The analyses were referred to the concentration found in samples and to those thresholds stablished by law. Most of the samples meet with the threshold stablished (Ecolabel in Europe), but in some of them (principally coated samples after weathering process) were detected higher concentrations than that allowed according to Ecolabel limits. The methodology used demonstrated to be effective in sorting polluted and non-polluted particles of some elements at high concentrations but at low concentration the accuracy is limited. These results are interesting to anticipate possible treatments of recycling at end of life or to take into account in the development of TMW protective products to keep it as a sustainable material.

INTRODUCTION

Thermal modification of wood is one successful environmental technology that combined temperature and moisture, avoiding the use of harmful substances, providing better energy efficiency and drying quality (Sandberg and Kutnar 2016). The wood quality of several fast-growing or non-durable wood species is improved by heat treatment process, adding commercial value to birch, ash, pine, oak or beech species and therefore opening their perspectives for use as building materials (Schultz and Nicholas 2007). Accordingly, it could be used as element for façades systems, terraces, urban furniture and windows (Militz and Altgen 2014).

On the other hand, modified wood surfaces exposed during service may present rapid drawbacks of visual appeal caused by weathering and/or biological decay. Finishing of wood surface with coating products has proved itself as a good solution to diminish the weathering effects and to maintain the aesthetical features when the material is exposed outdoor in different directions or designs.

The range of coating products used recently in the European market is dominated by the water-borne systems (Gennaro *et al*. 2015). These products (pigments or binders) are dispersed or dissolved in a continuous phase that consists essentially of water. Decorative coatings are usually applied by hand and are air-dried. In the contrary, industrial products use much wider range of application techniques and frequently require stoving or radiation curing (Bulian and Graystone 2009). Finally, an important consideration when applying any coating products is to avoid or substantially decrease emissions of the air polluting volatile organic compounds (Fellin *et al.* 2014). The goal of this study was to examine a response to artificial weathering of thermally modified wood coated with two different products, regarding the concentration of chemical elements in the samples before and after test.

EXPERIMENTAL

Wood material and industrial-scale treatment

Wood of European ash (*Fraxinus excelsior* L.) was thermally modified according to the state-of-the-art industrial production standards at 192, 202 ºC (Thermo-Drewno®, Poland) and 212 ºC (Termogenik®, Spain). The treatment was conducted with presence of saturated steam in dedicated heat-treatment processors. The treatment period was between 60 and 70 hours following the schedules of the industrial processes.

Wood finishing

All the wood surfaces were sanded before coating in order to assure minimal surface roughness, and improve adhesion with the coating. Two coating systems were used for the need of this research and the technical details are presented in Table 1.

Table 1: Coating application systems

Coating system	**Method**	**Thickness[1] [µm]**	**Density [g cm^{-3}]**	**Amount [g m^{-2}]**	**Drying**			**Curing**		
					Temp. **[°C]**	RH[2] **[%]**	Time **[h]**	UV-Lamp **[nm]**	UV-dose **[W cm^{-1}]**	Speed **[m min^{-1}]**
UV-hardened *(UV)*	*Industry*	1.Sealer:50	1.12	20	-	-	-	280-320[3]	80	10
		2·Clearcoat:10	1.18	20	-	-	-	280-320[3]	80	10
		3.Topcoat: 5	1.19	10	-	-	-	390-450[4]	120	15
2K waterborne *(WB)*	*Lab*	1.Primer: 90	0.88	100	20	50	18	-	-	-
		2.Topcoat: 60	1.04	100	20	50	5-6	-	-	-
		3.Topcoat: 50	1.04	100	20	50	200	-	-	-

[1] Theoretical value provided by producers; [2] RH= Relative Humidity; [3] Hg lamp; [4] Ga lamp

Accelerated artificial weathering

Coated wood samples after finishing and conditioning were exposed to the accelerated weathering test in order to simulate a combined effect of temperature, solar radiation and precipitation on the surface properties. The test was performed in a light exposure test apparatus (SOLARBOX 522, Erichsen) following standard procedure. Sample surfaces were cyclically exposed to 112 minutes of ultraviolet radiation (UVB-280 lamps) at 70 ºC (temperature on black panel), followed by 18 minutes of water condensation. The total duration of the weathering test was 2000 hours, what corresponded to 923 weathering cycles.

Chemical elementary composition in Energy dispersed X-ray fluorescence

ED-XRF analysis was carried out with an Oxford Instruments X-MET 5100, X-ray source set at 45 kV 40 lA (Figure 1). The measurement time is inversely proportional to the Limit of Detection (LoD); it has been set to 180 s according to the results of previous tests.

Figure 1: ED-XRF equipment used

RESULTS AND DISCUSSION

The results of the measurements before and after the accelerated weathering test are shown in Table 2. In this table, only the values within the limits detected by the equipment have been taken into account, and a correction has been made to detect and avoid the false positives.

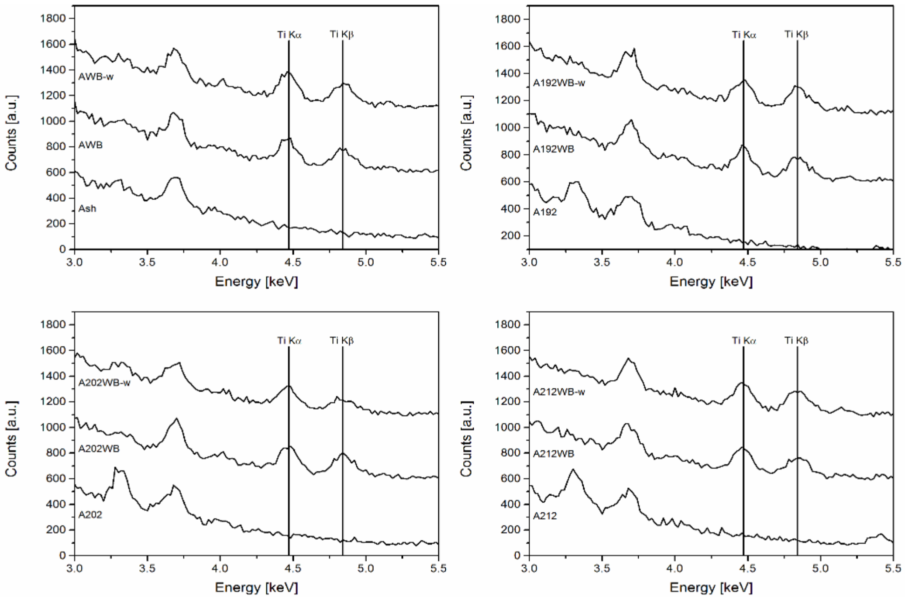
Table 2: Results of Multi-elemental analysis of the wood tested

Samples	Ca	Ti	Cr	Mn	Cu	Zn	Br	Sr	Ag	Cd	Ba
Ash	402.00 (43)	–	8.33 (2)	8.33 (1)	8.67 (≤0.5)	5.67 (≤0.5)	–	5.00 (≤0.5)	9.33 (2)	–	–
AUV	521.00 (44)	–	–	–	7.00 (≤0.5)	4.00 (≤0.5)	3.00 (≤0.5)	9.00 (≤0.5)	8.00 (2)	–	–
AWB	453.33 (43)	121.33 (10)	–	4.00 (1)	6.67 (≤0.5)	4.33 (≤0.5)	1.67 (≤0.5)	6.00 (≤0.5)	10.00 (2)	U.D.L	–
AUV-w	465.00 (44)	–	–	–	7.00 (≤0.5)	4.00 (≤0.5)	3.00 (≤0.5)	9.00 (≤0.5)	8.00 (2)	–	–
AWB-w	519.00 (44)	147.00 (11)	–	6.50 (1)	6.50 (≤0.5)	4.00 (≤0.5)	U.D.L	6.50 (≤0.5)	9.50 (2)	–	100.00 (30)
A192	444.80 (45)	–	14.40 (2)	6.20 (1)	7.20 (≤0.5)	4.80 (≤0.5)	–	2.20 (≤0.5)	5.20 (1)	U.D.L	–

Samples	Ca	Ti	Cr	Mn	Cu	Zn	Br	Sr	Ag	Cd	Ba
A192UV	323.00 (43)	–	–	7.00 (1)	8.00 (≤0.5)	6.00 (≤0.5)	11.00 (≤0.5)	3.00 (≤0.5)	9.00 (2)	–	–
A192WB	499.33 (42)	121.67 (10)	–	1.67 (≤0.5)	6.67 (≤0.5)	4.67 (≤0.5)	–	2.00 (≤0.5)	7.00 (1)	U.D.L	U.D.L
A192UV-w	382.00 (43)	–	–	5.00 (1)	7.00 (≤0.5)	4.00 (≤0.5)	–	2.00 (≤0.5)	10.00 (2)	–	–
A192WB-w	470.50 (44)	119.00 (11)	–	–	6.50 (≤0.5)	5.00 (≤0.5)	–	2.00 (≤0.5)	9.00 (2)	–	–
A202	553.33 (45)	–	6.00 (1)	6.67 (1)	7.67 (≤0.5)	6.33 (≤0.5)	–	4.67 (≤0.5)	8.67 (2)	5.33 (1)	–
A202UV	371.33 (43)	–	5.33 (1)	4.67 (1)	7.67 (≤0.5)	5.67 (≤0.5)	7.67 (≤0.5)	2.67 (≤0.5)	10.33 (2)	–	–
A202WB	559.00 (43)	141.00 (10)	–	3.67 (1)	6.00 (≤0.5)	4.00 (≤0.5)	–	2.33 (≤0.5)	5.67 (1)	–	–
A202UV-w	642.17 (45)	–	–	7.33 (1)	7.83 (≤0.5)	6.00 (≤0.5)	7.17 (≤0.5)	20.50 (≤0.5)	7.67 (2)	4.50 (1)	–
A202WB-w	454.00 (45)	109.00 (11)	–	7.00 (1)	6.00 (≤0.5)	6.00 (≤0.5)	–	3.00 (≤0.5)	9.00 (2)	11.00 (3)	–
A212	561.33 (45)	–	15.33 (2)	7.00 (1)	7.33 (≤0.5)	7.00 (≤0.5)	–	3.67 (≤0.5)	6.67 (1)	U.D.L	–
A212UV	634.33 (44)	–	–	7.00 (1)	7.33 (≤0.5)	7.33 (≤0.5)	6.67 (≤0.5)	19.67 (≤0.5)	9.33 (2)	–	–
A212WB	569.67 (44)	128.33 (10)	–	4.00 (1)	6.67 (≤0.5)	6.33 (≤0.5)	–	3.33 (≤0.5)	10.00 (2)	–	U.D.L
A212UV-w	328.50 (43)	–	5.50 (1)	7.50 (1)	6.50 (≤0.5)	5.00 (≤0.5)	12.00 (≤0.5)	2.50 (≤0.5)	8.00 (2)	6.00 (2)	–
A212WB-w	518.60 (44)	121.00 (10)	–	U.D.L	6.60 (≤0.5)	6.60 (≤0.5)	–	3.40 (≤0.5)	8.40 (2)	–	U.D.L

-w= Weathered, UDL= Under Detection Limits

Taking into account the experimental values obtained, the values of most of the detected elements are within the maximum permitted limits according to the community *Ecolabel.* However, it is appreciated that the titanium content in the surfaces treated with waterborne products is higher than the established as safe (2 -2.5 higher). Figure 2 shows the components (*ka*, *kb*) of the element that exceeds the limits (Ti) and its difference with natural wood. As for heat-treated wood surfaces, there are not significant differences in the concentration values



compared to non-heat-treated wood, indicating a retention within the ranges that natural wood can present.

Figure 2: Ka+ Kb of Titanium present in tested samples

CONCLUSIONS

Multi-element measurement of wood by ED-XRF technique was found to be effective, fast and reliable, and the results show that the concentration of titanium in the WB products exceeds the established limits but in a similar range for heat-treated wood as for natural wood.

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Thermowood® vs Termovuoto process – comparison of thermally modified timber in industrial conditions

Mohamed Jebrane[1], Ignazia Cuccui[2], Ottaviano Allegretti[2], Ernesto Uetimane Jr.[3] and Nasko Terziev[1]

[1] Department of Forest Products, Swedish University of Agricultural Sciences, Box7008, 750 07 Uppsala, Sweden, (e-mail: mohamed.jebrane@slu.se)

[2] CNR - IVALSA (National Research Council - Trees and Timber Institute), via Biasi 75, 38010 San Michele all Adige, Italy, (e-mail: cuccui@ivalsa.cnr.it; allegretti@ivalsa.cnr.it)

[3] Faculty of Agronomy and Forest Engineering, Eduardo Mondlane, University, Maputo, Mozambique (e-mail: wetimane@gmail.com)

Keywords: chemical analyses, durability, mass loss, mechanical properties, metil, neem, thermo-vacuum

ABSTRACT

The study aimed at treating Scots pine (*Pinus sylvestris* L.), spruce (*Picea abies* Karst.) and two hardwoods, metil (*Sterculia appendiculata* K. Schum) and neem (*Azadirachta indica* A. Juss) timbers in *industrial conditions* by steam (Thermowood®) and vacuum (Termovuoto) thermal modifications. Matched boards were treated identically and alterations in spectral characteristics and chemical composition of wood were compared. Mass loss, selected mechanical properties and wood durability were also traced and related to the chemical alterations. The physical nature of the two processes induced similar changes in chemistry and structure of softwoods but at different magnitudes for the hardwoods. The applied vacuum removed partly the acetic acid, which catalysed carbohydrate degradation, i.e. heat applied under vacuum was less destructive. Wood permeability was found important in the thermo-vacuum process.

Mass loss was significantly higher after Thermowood® process namely, 14.1% vs. 9.9% for metil and 14.2 and 12.1% for neem wood. No significant mass loss differences were found between pine and spruce wood after the two treatments. Mass loss correlated with the decrease of shear strength, rupture and elasticity moduli and increase of wood decay resistance. As more permeable, metil demonstrated significant difference between the properties above; thermo-vacuum process was less destructive but ensured lower improvement of durability compared to Thermowood® treatment.

The entire study allows concluding that Thermowood® and thermo-vacuum treatment according to Termovuoto technology produce similar final products with regard to chemical, physical-mechanical properties and durability with clear difference in the appearance (colour). Thermo-vacuum modification of wood can be advantageous where the end use of the product demands retaining the mechanical properties closer to those of the untreated material.

The work was performed in the framework of the Eco-Innovation initiative EU project TV4NEWOOD ECO/12/333079 and supported by the Swedish Research Council (Vetenskapsrådet).

INTRODUCTION

Termovuoto (TV) process is a new industrial thermal modification (TM) technology that has been developed by the National Research Council of Italy and SLU, Sweden, based on the combination of an efficient vacuum drying process with thermal treatment process (Allegretti *et al*. 2012, Ferrari *et al.* 2013). It is actually a thermo-vacuum process where the wood is dried initially in air at 100°C until the moisture content reaches 0%. Thereafter, TM is performed in the same chamber by increasing the temperature in the range of 160-220°C. A vacuum pump is used at this time to remove the residual air and maintain the vacuum. Compared to other TM processes, TV is a promising method with several advantages such as shorter duration and lower energy consumption, easier and cheaper management of the volatile waste and less corrosive. Lower mass loss of wood and odourless final product that might be affected by the action of the vacuum pump that continuously removes volatile compounds are other important features of TV (Allegretti *et al.* 2012, Candelier *et al.* 2013a,b). Several TMWs produced by TV process from softwoods and hardwoods have already been found to yield satisfactory mechanical properties and decay resistance. Commercially treated wood is already available on the market under the name *VacWood.*

The objective of the study was to compare selected chemical, physical-mechanical properties and durability of Scots pine (*Pinus sylvestris* L.), Norway spruce (*Picea abies* Karst.), metil (*Sterculia appendiculata* K. Schum) and neem (*Azadirachta indica* A. Juss) timber modified in *industrial conditions* by steam according to Thermowood® technology (TW) and under vacuum by Termovuoto process (TV). The comparison was intended to find out the features of modified wood and reveal eventual differences that may be caused by the nature of the applied processes. The choice of the wood species reflects the most commercially used and thermally modified timbers in Europe but also example of two tropical hardwood timbers.

EXPERIMENTAL

Sampling and thermal modification: Three logs of Scots pine, spruce, metil and neem were sawn to boards (28×120×3100 mm) that were stored and dried in room climate for 2 months. Six boards of each wood species were chosen for the present experiment and cut to 3 sub-samples (28×120×1000 mm); the first two sub-samples were treated by TW and TV methods while the third sub-sample served as untreated control. Wood density at room climate was determined and a 10-mm thick slice was cut from each sub-sample for initial moisture content (MC). In order to ensure comparability between the two treatments, both TW and TV thermal modification consisted of *a) initial drying* to achieve very low MC prior to the real thermal treatment; *b) heating phase from 100°C and up* to the target temperature set value with an approximate increase of 10ºC/h; *c) thermal modification phase* at constant temperature of 212°C and duration of 3 h; and *d) cooling phase* to slow down the wood temperature to 50°C. The experiments were carried out in *industrial TM chambers* of ca. 10 m^3 volume.

Lignin, monosaccharides and acetyl content: Treated and untreated samples were analyzed for soluble lignin (L), monosaccharides and acetyl content (Ac) based on acid hydrolysis. L was determined by Hitachi U-2910 spectrophotometer with an absorptivity of 110 L/g cm at 205 nm. The monomeric carbohydrates were determined by a HPLC system equipped with an evaporative light scattering detector (ELSD-90), and a Metacarb 87P column (300×6.5 mm) with a guard column (Metacarb 87P 50×4.6 mm). The ELSD-90 was operated at 50ºC, 2.5 bars and N_2 was used for spray forming. The sugars were eluted by ultra-pure water as mobile phase at a constant flow rate of 0.5 mL/min at 85ºC. The acetyl content was determined by means of a diode array detector (DAD) operated at 210 nm, and a Metacarb 87H column combined with a guard column (MetaCarb 87H 50×4.6 mm). The mobile phase was 0.005 mol/L H_2SO_4 (pH 2.1), with a flow rate of 0.6 mL/min at 30ºC.

Mass loss (ML) and colour evaluation: All boards were weighed after treatments and ML was calculated (Table 2). Five boards of each species and treatment were randomly selected and color measurements carried out on board areas without defects. Konica Minolta CM-2500d surface reflectance spectrophotometer was used, the colour space coordinates L^*, a^* and b^* measured and colour difference (ΔE^*) calculated.

Mechanical properties: Untreated and treated samples were conditioned to the same MC (*ca.* 8%) prior to the mechanical tests which were carried out by a testing machine (Shimadzu AG-X 50 KN) with accuracy of ±0.01 mm for position, ±0.1% for speed, and ±0.5% for loading. The measured properties were modulus of elasticity (MOE), modulus of rupture (MOR), static hardness perp. and parallel to grain, compression stress perp. and parallel to grain and shearing strength parallel to grain, all measured according to ISO standards.
Durability test with basidiomycetes: Wood durability classes were obtained by laboratory tests with white and brown rot fungi (EN 113 2004). Decay fungi: *Coniophora puteana* BAM Ebw. 15, *Gloeophyllum trabeum* BAM Ebw. 109, *Postia placenta* FPRL 280 and *Trametes versicolor* CTB 863A. Prior to the test, the treated samples were leached in water. The durability class is derived from the ratio of $ML_{sample}/ML_{reference}$.

RESULTS AND DISCUSSION

Compared to the untreated wood, the sum of simple sugars from hemicelluloses decreased significantly after both treatments (Table 1).

Table 1: Chemical constituents (%) of untreated and thermally modified soft- and hardwood samples (UN – untreated, TW – Thermowood treated, TV – thermo-vacuum treated)

Species	UN	TW	TV	Difference TW-TV
			Hemicelluloses	
Neem	17.2	9.0	8.5	0.5
Metil	14.7	5.1	9.1	-4.0
Pine	24.3	16.9	18.2	-1.3
Spruce	23.5	15.4	18.6	-3.2
			Acetyl content	
Neem	7.0	4.4	5.2	-0.8
Metil	8.2	4.4	5.7	-1.3
Pine	2.6	2.3	2.4	-0.1
Spruce	2.9	2.6	2.8	-0.2
			Lignin	
Neem	28.2	39.9	31.2	8.7
Metil	24.1	33.8	24.2	9.6
Pine	26.6	32.5	31.2	1.3
Spruce	27.8	31.0	29.8	1.2

The decrease caused by TW was larger than that of TV; the hemicellulose difference between TW and TV was particularly large for spruce and metil, i.e. TV causes less degradation of the hemicelluloses (Table 1). Similar results (Candelier *et al.* 2013a) were reported for thermally modified beech in nitrogen under vacuum. The degree of hemicelluloses degradation is proportional to the Ac decrement, which was clearly seen for all species and both treatment methods; the decrease was more pronounced after the TW process and thus, the hypothesis of the effect of vacuum during TM can be confirmed. As shown by Fengel and Wegener (1989), wood polysaccharides are affected by the presence of acetyl groups that are thermally labile and lead to formation of acetic acid, thereby causing acid-catalysed degradation of the polysaccharides during TM. The results showed neither significant decrease in Ac between untreated and modified and spruce, nor between the TW and TV treatments. On the other hand, hardwoods, particularly metil, were more liable to acid-catalysed degradation. This is explained by the fact that softwoods have lower hemicellulose content than hardwoods and the hemicelluloses of softwoods have a lower Ac compared to hardwoods. The thermal degradation of softwoods at defined temperature and duration is expected to be less compared to hardwoods (confirmed by the ML in Table 2). L content for all species is elevated (Table 1), while the L increment in case of TW process is significantly higher for the hardwood species. Material's ML is reflection of the chemical changes caused by the TM; in this study the effect of TM was proven by high ML (>7%) for all tested species (Table 2).

Table 2: Density (kg/m3), mass loss (ML, %) of thermally modified soft- and hardwood boards and colour difference ΔE* (UN – untreated, TW – Thermowood treated, TV – thermo-vacuum treated).

Species	**Density UN**	**ML_{TW}**	**ML_{TV}**	**Difference TW-TV**	**ΔE^* (TW-TV)**
Neem	702	14.2	12.1	2.1*	3.7
Metil	589	14.1	9.9	4.2*	6.0
Pine	409	9.3	9.0	0.3	3.0
Spruce	402	7.1	7.5	-0.4	5.7

** Statistically significant difference (t-tests at α = 0.01)*

TW caused significantly higher ML than TV in both hardwoods, while the ML difference in the softwoods was insignificant (Table 2), i.e. the result does not support earlier reports (Allegretti *et al.* 2012) and results (Candelier *et al.* 2013a,b). In the case of softwoods (pine and spruce), we presume that during TM, the permeability of pine and spruce is similar and low since neither pine nor spruce was subjected to stronger thermal degradation by the TW process compared to TV (Table 2).

The ML of TW metil and neem are similar (14.1 and 14.2%, respectively). The effect of vacuuming away the acetic acid during the course of TM is expected to be stronger in more permeable wood species (i.e. less ML in metil than neem) confirmed by the results in Table 2 (9.9% for metil vs. 12.1% for neem). Metil is diffuse-porous wood with 371 µm average vessel diameter at a frequency of 5 per mm^2; it lacks tyloses or any visible incrustations in the vessels. Its thin-walled axial and ray parenchyma constitutes the bulk of the ground tissue. Thus, metil wood is lighter than neem and has a high impregnability as demonstrated by a high liquid uptake of 463 kg/m^3. Neem is also diffuse-porous wood with significantly smaller vessel diameters (up to 80 µm) and the vessels dispose of simple perforated plates, on which reddish-brown deposits of gum are visible and plug the perforations. The decrease in permeability in some hardwoods is caused by deposition of extractives on vessel perforations and cell walls blocking fluid transfer through the porous media. Higher density of neem and its smaller vessels with deposits on the perforation plates indicate a lower permeability than in metil. This explains why the degradation products are removed easier from metil than from neem. Consequently, neem suffers higher ML in TV treatment than metil while in TW the ML of the two species are similar (Table 2).

TW treated wood is visible darker than the TV wood for all tested species. The colour difference *ΔE** is larger for metil and spruce than for neem and pine, as seen by naked eyes (*ΔE**> 3). The lighter colour of TV wood correlates well with its lower ML (Table 2). Gonzalez-Pena and Hale (2009) found that *ΔE** is a good predictor to describe even reduction of a number of mechanical properties of TM beech, Scots pine and spruce, contrary to Johansson and Moren (2006) who found weak colour-to-strength relationship. When TW and TV methods are compared by the mechanical properties, it is apparent that only MOR of pine differs significantly (Table 3).

Table 3: Mechanical properties (N/mm2) of untreated and treated samples that are significantly different between TW and TV treated wood. (UN – untreated, TW – Thermowood treated, TV – thermo-vacuum treated).

Species	UN	TW	TV	Difference TW-TV
		MOE		
Metil	9617	6396	7262	-866
		Shear strength		
Metil	11.2	6.7	8.7	-2.0
		MOR		
Metil	99	46.7	57.6	-10.9
Pine	85.1	62.8	73	-10.2

The value is larger for wood treated by TV than TW. The ML of the softwoods in this study is similar after TW and TV treatment processes and thus, there is no reasonable explanation why MOR deviates from the general trend. For the hardwoods, only some features of metil demonstrated significant difference between the methods; MOE, shear strength and MOR decreased more for TW treated wood than that treated by TV. Permeability of the treated wood species probably matters significantly when TV is applied; metil is a permeable species, and thus the acetic acid produced is easily removed leading to less ML at the end of the treatment. In absence of acetic acid, the MOE, MOR and shear are higher than after TW. Durability improvement of metil (DC 3) after TV is also less than after TW treatment (Table 4).

Table 4: Durability classes (DC) of untreated and treated samples exposed to basidiomycete fungi in a standard EN 113 test. (UN – untreated, TW – Thermowood treated, TV – thermo-vacuum treated).

Species	DC_{UN}	DC_{TW}	DC_{TV}
Neem	3	1	1
Metil	5	2	3
Pine	4	2	2
Spruce	4	2	2

The effect of TM on wood durability does not vary between pine, spruce and neem. TV modification shifts up the wood durability with two classes above the initial natural DC (Gao *et al.* 2016) which is also confirmed in the present study.

CONCLUSIONS

Thermowood® and TV treatment Termovuoto of Scots pine, Norway spruce, metil and neem timber ensure similar final products. Performed at identical temperature and duration, Thermowood® and TV process caused similar mass loss of the softwood species. Chemical analyses showed decreased hemicellulose content in both softwood species, while no significant effect on the acetyl content was observed. Hardwood (metil), mechanical and durability tests confirmed the basic role of the ML caused by the TM as an indicator of wood's physical and mechanical properties and durability. Wood permeability is an important factor in the TV process that should be considered when wood species are selected for treatment. The study concludes that Thermowood® and Termovuoto technology produce similar industrial products regarding chemical, physical-mechanical properties and durability with some difference in the appearance.

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Study on Drying Characteristics of Poplar Wood Impregnated with Urea-formaldehyde Resin

Yang Lihu[1] and Yuan Haiguang[2]

[1]Hebei AMS, Handan,CN-056800, Hebei [email: ams.caroline@hotmail.com)]
[2]Jiangsu AMS, Huaian, CN-223001, Jiangsu[email: imyuany@163.com)]

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ABSTRACT

Drying characteristics of Poplar wood impregnated with urea-formaldehyde resin were analyzed by using the 100-degree Celsius test. The results showed the drying characteristics difference between impregnated wood and untreated wood. Poplar wood impregnated with wood resin had no initial cracking and internal cracks, a slight distortion in cross section, but shrinks easily, with great difference in drying shrinkage in tangential and radial directions than untreated poplar wood, and it dried significantly slower than untreated wood.

INTRODUCTION

Fast-growing *poplar* has certain disadvantages including low density (basic density 0.35g/cm^3), soft and with light colour, high and unevenly distributed moisture content, a multi-stress wood, which shrink and deform easily, among others, thus limit its direct use and cannot be used to produce high-quality and high value-added wood products. After the wood is impregnated with resin, its physical and mechanical properties are largely improved, giving the ordinary poplar a much wider scope of application. The impregnation process involves two rounds of drying to remove moisture and also let the urea-formaldehyde resin inside the wood curing and strengthen the bond between wood cells. Currently, there are relatively few studies on the drying characteristics of impregnated poplar wood.

The 100-degree Celsius drying test is commonly used for preliminary exploration of drying characteristics of raw sawn timber during the drying process. It is a simple, convenient and practical method. In this experiment, the test was used on impregnated poplar wood and untreated poplar wood to investigate their drying properties, thereby provide relevant reference for industrialized production.

EXPERIMENTAL

Materials

Impregnated poplar wood timber

Sourced from Hebei AMS Wood Processing Co., Ltd. and impregnated with urea-formaldehyde resin approximately 30%. 9 pieces of test specimens, 700mm long, 150mm wide, 25mm thick, chord wise planed, straight grain texture and no surface defects, initial moisture content was about 72%.

Untreated poplar wood timber (control material)

Untreated wet raw material, from the same company mentioned above, 7 pieces of specimens, length 700mm, width 150mm, thickness 25mm, chord wise planed, straight grain texture and with no surface defects, initial moisture content was about 80%.

Before the drying test, the impregnated poplar wood and the untreated poplar wood were planed and flat-sawn to 7-9 200 mm×100 mm×20 mm pieces.

Test equipment

High-precision woodworking saws, electric thermostatic blast drying oven, electronic balance with precision 0.01g, electronic verniercaliper with precision 0.01mm, stainless steel ruler with precision 0.5mm, feeler gauge with precision 0.01mm and relevant others.

Test method

Impregnated poplar and untreated poplar wood were divided into two groups and tested using the 100-degree Celsius method.

RESULTS AND DISCUSSION

Test result and defect statistics

Test findings and statistics of the impregnated poplar and untreated poplar wood (defects found and grading) are shown below (Table 1, Table 2, Table 3 and Table 4).

Table 1: Defects and defect grading of impregnated poplar

NO.	Initial crack	Grade	Inner crack	Grade	Section deformation [mm]	Grade	Distortion [mm]	Grade
A1	No	1	No	1	0.16	1	0.5	1
A2	No	1	No	1	0.34	1	0.9	2
A3	No	1	No	1	0.66	2	2	2
A4	No	1	No	1	0.32	1	1.8	2
A5	No	1	No	1	0.44	1	3	2
A6	No	1	No	1	0.35	1	2	2
A7	No	1	No	1	0.59	2	1.5	2
A8	No	1	No	1	0.3	1	4	3
A9	No	1	No	1	0.43	1	2	2

Table 2: Defects and defect grading of untreated poplar

NO.	Initial crack	Grade	Inner crack	Grade	Section deformation [mm]	Grade	Distortion [mm]	Grade
B1	Yes	1	No	1	0.65	2	1.5	2
B2	Yes	2	No	1	0.9	2	2.5	2
B3	Yes	3	No	1	0.51	2	3.5	3
B4	Yes	3	No	1	0.68	2	2.3	2
B5	Yes	2	No	1	1.38	3	2	2
B6	Yes	1	No	1	1.02	3	1	2
B7	Yes	2	No	1	0.74	2	1.5	2

Table 3: Drying speed of impregnated poplar

NO.	Drying speed[a] [h]	Drying speed[b] [%/h]	Grade
A1	23	1.05	4
A2	24	1.26	4
A3	14	1.89	2
A4	23	1.62	4
A5	24	1.14	4
A6	15	1.21	3
A7	16	0.92	3
A8	18	1.04	3
A9	16	0.95	3

[a]Time taken for the moisture content decrease from 30% to 5%.

[b]The moisture decrease percentage per unit time, from 30% to 1%.

Table 4: Drying speed of the untreated poplar

NO.	Drying speed[a] [h]	Drying speed[b][%/h]	Grade
B1	8	1.19	1
B2	8	0.96	1
B3	9	1.18	1
B4	10	1.22	1
B5	9	0.93	1
B6	8	1.11	1
B7	8	1.12	1

[a]Time taken for the moisture content decrease from 30% to 5%.

[b]The moisture decrease percentage per unit time, from 30% to 1%.

Drying characteristics analysis

Initial crack

Table 1 and 3 show resin-impregnated poplar wood did not crack during the 100-degree Celsius drying process, only a thin end shake of about 9 mm occurred, defect of grade 1.

Table 2 and 4 show the untreated poplar did not crack within 1h. After drying for 2h, up to 28 end-cracks of different grades; 5 surface cracks of up to 10mm. The cracks gradually widened and increased and were the worst after 6h, with 28 end-cracks of width up to 1.52 mm and 3 surface cracks length 17.88mm, 7.00 mm and 5.00 mm. After 11h, most of the end-cracks began to shrink and surface fissures healed, the widest end-crack among 24 was 0.78 mm and the 1 surface crack was 18.84 mm long. After 24h, most of the end cracks healed or became smaller. Some specimens warped and shrank partially, the best specimen had only 9 thin end cracks and no surface crack. After 30h, the specimens showed no further change, with the best having only 5 thin end clefts and no surface cracks. The test found that the untreated poplar initial cracking were severe and the defects averaged grade 2.

Analysis: The urea-formaldehyde resin impregnated into the poplar wood was cured during the drying process which hindered the movement of moisture to a certain extent and reduced the drying stress markedly, so no cracking occurred.

Inner crack

The above tables showed that there was only one short inner crack in one of the 9 impregnated poplar wood specimens, and there was no internal crack in the seven specimens of untreated poplar. Both group A and B were defined as grade 1.

Section deformation

The above tables show that section deformation of impregnated poplar were basically within 1.0mm, defined as grade 1; untreated poplar 0.5-1.5mm, 5 specimen grade 2 and 2 specimen grade 3. Section deformation is affected mostly by the initial drying temperature and humidity, and relative less by final humidity, therefore by adjust initial drying stage temperature and humidity, section deformation can be reduced.

Twisting

Table 1 and 2 show that treated poplar twisted maximum 4 mm, untreated poplar 3.5 mm, both grade 2. The twisting was mainly due to the natural wood longitudinal texture is not straight, it can be reduced by high temperature and humidity treatment at the start of the drying process or by weighing down heavy on the material.

Drying speed

Table 3 shows group A took 18.33h for the moisture decrease from 30% to 5%, on average 1.23%/h from 30% to 1%, with drying speed varying, average grade 3. Table 4 shows group B, the 7 untreated poplars took 8.57h from 30% to 5%, 1.10%/h from 30% to 1%, with drying speed relatively uniform, average grade 1. The untreated poplar wood dried obviously faster than the impregnated poplar wood.

Drying speed is an important indicator of moisture movement and the difficulty of wood drying. It’s mainly related to the wood structure. Since the urea-formaldehyde resin impregnated in the wood curing during the drying process and blocked moisture movement, the treated wood dried slower.

Shrinkage characteristics

Shrinkage of the wood in the drying process affects cracking and warping, *etc*. Statistics of the shrinkage properties of the two kinds of specimens are shown in (Table 5).

Table 5: Drying and shrinking properties at 100°C

Sample	Specimen number	Chordwise shrinkage [%]	Radial shrinkage [%]	Volume shrinkage[%]	Differential shrinkage[%]
Impregnated poplar	Average	2.64	0.89	3.51	3.23
	Variation	9.34	31.86	9.90	28.25
Untreated poplar	Average	4.16	1.94	6.02	2.20
	Variation	23.87	19.21	18.76	27.39

The test found the impregnated poplar wood shrink significantly less than untreated poplar in the drying process, but the ratio of tangential to radial shrinkage was bigger, indicating that resin treated poplar was more tend to warp and crack in drying process.

Draw up drying standards

Basic drying conditions

The drying conditions corresponding to the respective defect grades of resin impregnated poplar and untreated poplar ascertained in the 100-degree Celsius test are presented below (Table 6).

Table 6: Drying conditions corresponding to the defect grade of the sample

Drying defects	Impregnated poplar			Untreated poplar		
	Initial crack	Section deformation	Inner crack	Initial crack	Section deformation	Inner crack
Grade	1	1	1	4	2	1
Initial temperature [℃]	70	70	70	50	60	70
Dry & wet bulb difference [℃]	7	7	7	2	5	7
Max. temperature [℃]	95	95	95	80	80	95

According to the comprehensive drying conditions (Table 6), the resin treated poplar wood had less defects than untreated wood, but dried slower. This indicated that the urea-formaldehyde resin inside the impregnated poplar to an extent impeded moisture movement in the wood. Therefore, the drying stress reduced greatly and the drying defects were less than the untreated poplar.

Drawing up drying Standards

According to the initial temperature, humidity and final temperature of the specimens and the LY/T 1068-2012 Technology Rules of Kiln Drying Swan Timber, the proposed drying standards for 25 mm resin treated and untreated poplar wood as below (Table 7).

Table 7: Proposed drying standards

Impregnated poplar			Untreated poplar		
Moisture [%]	Dry bulb temperature [℃]	Wet bulb temperature [℃]	Moisture [%]	Dry bulb temperature [℃]	Wet bulb temperature [℃]
＞50	70	63	＞50	50	48
50-40	72	63	50-40	52	48
40-35	74	62	40-35	54	49
35-30	76	62	35-30	58	50
30-25	80	62	30-25	64	52
25-20	85	62	25-20	72	54
20-15	90	62	20-15	77	54
＜15	95	60	＜15	80	54

Impregnation treated poplar wood filled with resin that has certain influence on the moisture movement. At the beginning of drying should use low temperature to prevent rapid evaporation of moisture with resin before it curing, meanwhile, to avoid the resin curing too early and obstruct moisture discharge from the wood. Through the actual drying process as the drying standards (Table 7), resin loss seriously from the impregnated poplar in the initial stage, the actual weight gain percentage was less than the theoretical level, it means there was an impact on the impregnation effect.

In order to reduce the resin loss, the proposed drying standards needed to be revised. The lower temperature to the initial drying of the processed material can reduce the loss of the resin. In the later stage of drying, high temperature is required to help the resin curing, hence the temperature of the kiln in later stage drying should be increased as the heating capacity of the kiln allows. The untreated poplar retained its good quality in the actual drying process, indicating that the benchmarks set were on the slack side and needed to be tightened. The revised standards are shown as following (Table 8).

Table 8: Revised drying standards

Impregnated poplar			**Untreated poplar**		
Moisture [%]	**Dry bulb temperature [℃]**	**Wet bulb temperature [℃]**	**Moisture [%]**	**Dry bulb temperature [℃]**	**Wet bulb temperature [℃]**
＞50	53	51			
50-40	54	52	50-40	55	52
40-35	55	52	40-35	58	53
35-30	60	55	35-30	63	55
30-25	65	56	30-25	70	56
25-20	70	56	25-20	75	57
20-15	80	62	20-15	78	57
＜15	90	60	＜15	82	57

CONCLUSIONS

The drying characteristics of urea-formaldehyde resin impregnated wood and untreated poplar wood are notably different. The impregnated poplar dries slower, but the resin in it curing during drying, resist crack or less deformation than untreated poplar.

Impregnation treated wood had no initial cracking and internal cracking in the drying process, section deformation was grade 1; whereas untreated wood with serious initial cracking of grade 4 or 5, section deformation grade 2 ; both distorted grade 2.

The resin treated whole dry poplar wood’s average shrinkage chordwise 2.64%, radial 0.89%, volume 3.51%, differential 3.23%. The untreated poplar chordwise 4.16%, radial 1.94%, volume 6.02%, differential 2.20%. The test found that the impregnated poplar shrinks significantly less than untreated poplar, but greater differential, indicating resin treated poplar was more tend to warp and crack in drying process.

The results in the experiment are for reference only. For large-scale production, further tests and adjustments should be undertaken according to the drying kiln used.

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Life cycle assessment of bio-based façades during and after service life: maintenance planning and re-use

Marta Petrillo[1], Jakub Jakub[2,3,4], Anna Sandak[5], Paolo Grossi[6] and Andreja Kutnar[7,8]

[1]CNR-IVALSA, via Biasi 75, 30010 San Michele all’Adige, Italy [email: petrillo@ivalsa.cnr.it]
[2]InnoRenew CoE, Livade 6, 6310 Izola, Slovenia [email: jakub.sandak@innorenew.eu]
[3]CNR-IVALSA, via Biasi 75, 30010 San Michele all’Adige, Italy [email: sandak@ivalsa.cnr.it]
[4]University of Primorska, Faculty of Mathematics, Natural Sciences and Information Technology, Glagoljaska 8, 6000 Koper, Slovenia
[5]CNR-IVALSA, via Biasi 75, 30010 San Michele all’Adige, Italy [email:anna.sandak@ivalsa.cnr.it]
[6]CNR-IVALSA, via Biasi 75, 30010 San Michele all’Adige, Italy [email: grossi@ivalsa.cnr.it]
[7]InnoRenew CoE, Livade 6, 6310 Izola, Slovenia [email: andreja.kutnar@innorenew.eu]
[8]University of Primorska, Andrej Marušič Institute, Muzejski trg 2, SI-6000 Koper,Slovenia [e-mail: andreja.kutnar@upr.si]

Keywords: bio-based material, cascading, end-of-life, façade, life cycle assessment, re-use, service life

ABSTRACT

New developments in the field of wood protection, coupled with the European political determination to lower the environmental impact of the building sector, designates wood and bio-based materials as an excellent option for building façades. Despite that, the share of wood in the European wood construction market is low, with the exception of some North European countries. For that reason, it is necessary to increase a confidence in bio-based façades by demonstrating their environmental performances during and after the service life by means of solid scientific tools and experimental evidences. As a pilot study, we investigated the interactive LCA in two maintenance scenarios (high and low intensity), assuming two diverse cladding bio-materials (untreated sawn wood and chemically modified wood). A dedicated software tool was developed for the needs of these analysis allowing dynamic simulation of environmental impact and immediate visualization of the LCA contributions. The end-of-life options were assessed with a different approach. Firstly, several alternative scenarios for re-use that are available on the market were identified and listed. Secondly, we established a weight-based expert system expressing importance/advantage of each scenario in order to classify each end-of-life option according to its provision of environmental benefit. Finally, we assessed the suitability of each defined end-of-life option for all evaluated bio-based materials.

INTRODUCTION

The construction sector represents a large proportion of the consumption of the earth's non-renewable resources in terms of materials used for construction and energy consumption for operation of buildings. Aggregate, concrete and bricks are the most used construction materials in Europe, covering 45%, 42% and 6.7% of the total volumes respectively. At the same time, the share of timber structures accounts for only 1.6% of the total (Herczeg *et al.* 2014). Energy consumption of buildings in developed countries comprises 20-40% of the total energy use, more than industry and transport sectors (Pérez-Lombard *et al.* 2008). To reduce the use-phase costs of buildings, the selection of optimal building envelope systems can be crucial. However, materials for building envelope can have a high manufacturing costs (both economic and environmental). It is reported in several studies that the bio-based building materials have lower embodied energy than traditional ones (Kovacic *et al.* 2016, Lugt and Bongers 2016, Lupíšek *et al.* 2015, Werner and Richter 2007, Zabalza Bribián *et al.* 2011). Moreover, as bio-based materials are renewable, these are suitable at the end of service life for diverse paths of re-use (Thonemann and Schumann 2018). In spite of the economic crises, the production of some now well-established engineered wood products for structural use, such as cross-laminated timber (CLT), is intensively growing in Europe and globally (Brandner *et al.* 2016). Moreover, the improvements of the new wood-based products make these suitable to substitute some fossil-based raw materials. It is foreseen that there is a potential to doubling the added-value of the wood industry by 2030 (Hetemäki and Hurmekoski 2016). Furthermore, recent technological developments allow mass production of wood-based products (modified wood) that still few years ago were at the prototype stage (Mantanis 2017, Sandberg *et al.* 2017). The environmental impact of the production phase is disclosed for some modified wood products in dedicated EPD documents or LCA-related literature. For example, the carbon footprint of 1 m^3 of chemically modified wood can vary between 258 and 511 kg CO$_2$eq (Lambert and Daae 2015, Vogtlander 2015), while that of 1 m^3 of thermally modified wood can be between 131 and 133 kg CO$_2$eq (Ferreira *et al.* 2018). Nevertheless, the data differ greatly based on wood species, process-specific inputs and outputs, type of production plant, transportation, among the others. The environmental impact of the service life of wood-based façades has been rarely assessed, also because it is complicated to properly define the service-life duration, the limit state for maintenance operations and, consequently, to calculate the maintenance frequency (Grüll *et al.* 2011). In order to fill this gap, we developed a software tool that calculates the environmental impact of the maintenance of wood-based façades. The system was tested on two case scenarios of maintenance: high frequency/intensity and low frequency/intensity for two diverse wood-based façade solutions.

EXPERIMENTAL

Life cycle assessment (LCA) method was applied to four elementary maintenance operations typically executed on façades: cleaning, sanding, recoating and replacing (Petrillo *et al.* 2018). Figure 1 presents a graphical representation of the abovementioned operations/modules, including summary of the life cycle inventory data as used for environmental impact computation. All the modules can be combined together in an interactive LCA, where the user can define several variables describing the real-life scenario of the façade usage. The intensity of maintenance, material performance, local macroclimate as well as the owner’s tolerance for aesthetical deficiencies are particularly important factors affecting the LCA results. We tested the cleaning operations considering both presence or absence of a detergent in addition to the water. Therefore, the output can be only water or water contaminated with the detergent. These two options were tested in two different scenarios. The use of electricity was included to account for the use of pressure-machine (power 1,5-2 kW, work efficiency 0,015-0,025 h/m^2) in the cleaning operations. The sanding operations include sandblasting with pressure machine (power 1,5-5,5 kW, work efficiency 0,025-0,008 h/m^2) and a natural abrasive media, such as corn cob or walnut shells. The type of waste flow can be different: only sawdust in the case of sanding natural, untreated wood, sawdust and waste paint in the case of coated wood, sawdust with chemicals in the case of impregnated wood. Three scenarios were calculated considering the re-use of the abrasive media. Usually, this operation is a preliminary step before re-coating.

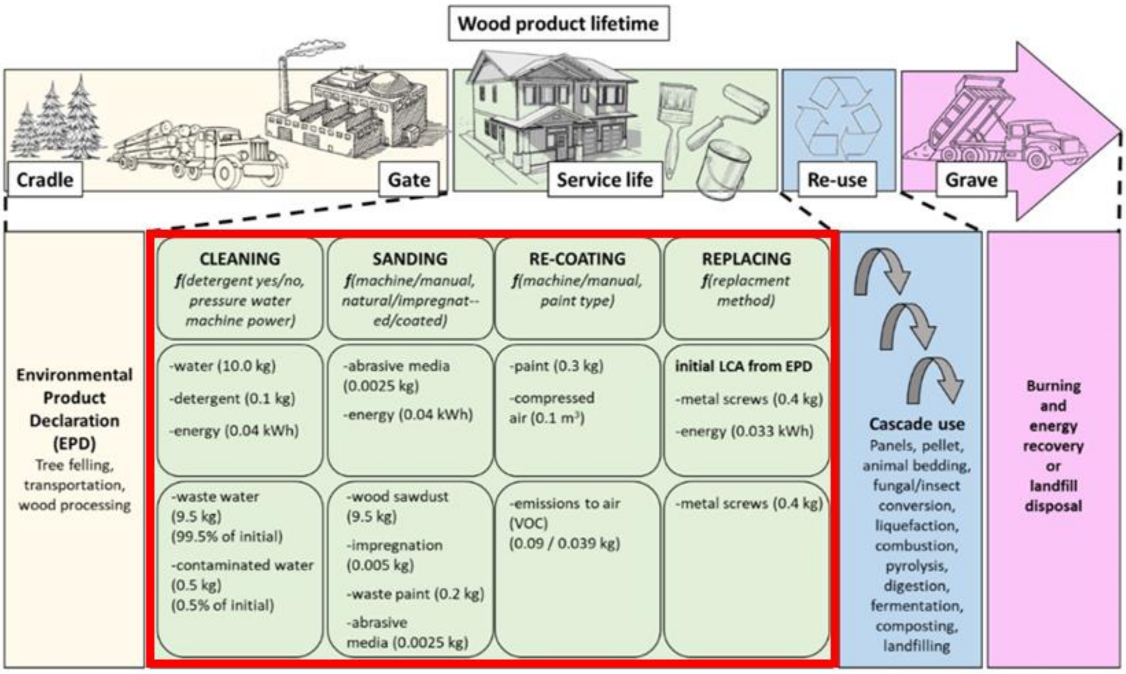

Figure 1: Lifetime of wood products with emphasis on service life. Maintenance modules are described in terms of input and output of materials and natural resources (life cycle inventory) (Petrillo et al. 2018).

The options for re-coating were based on acrylic and alkyd paints, water- or solvent-based. Moreover, all paint types were calculated for the options: hand-painting or machine-painting (spray-machine with compressed air). For the replacement operations, we considered the substitution of 25% of the façade in terms of the new material (data from available EPDs) and the environmental impact of the operations for replacement (metal screws, screwdriver energy demand). Then, we hypothesised two maintenance scenarios: high level of maintenance, due to harsh climate and high esthetical standard, and low level of maintenance, due to mild climate and low aesthetical standard. Based on practitioners' experience, scientific literature and technical data provided by material producers, we defined the maintenance options and their frequency in the four cases, as represented in Table 1.

Table 1: Condition for simulation of four case scenarios in 20 years of service life

	Case 1	**Case 2**	**Case 3**	**Case 4**
Climatic conditions	Harsh	Mild	Harsh	Mild
Material type	Natural wood (conifer)	Natural wood (conifer)	Chemically modified wood	Chemically modified wood
Owner aesthetical standard	High	Low	High	Low
Cleaning (times in 20 years)	6	2	9	3
Sanding + Re-coating frequency (times in 20 years)	2	1	0	0
Replacing frequency (times in 20 years)	1	0	0	0

Finally, we defined a system to weight different end-of-life (EOL) scenarios. The system takes into account for each EOL option the factors which are relevant for the calculation of LCA, such as: the potential for multiple re-use, the demand of additives for the new use, the energy required for the process and, finally, the possibility to recover energy at the end of the re-use cascade.

RESULTS AND DISCUSSION

The results indicate that the environmental impact of the use phase can vary greatly due to the climate and user, as represented in Figure 2.

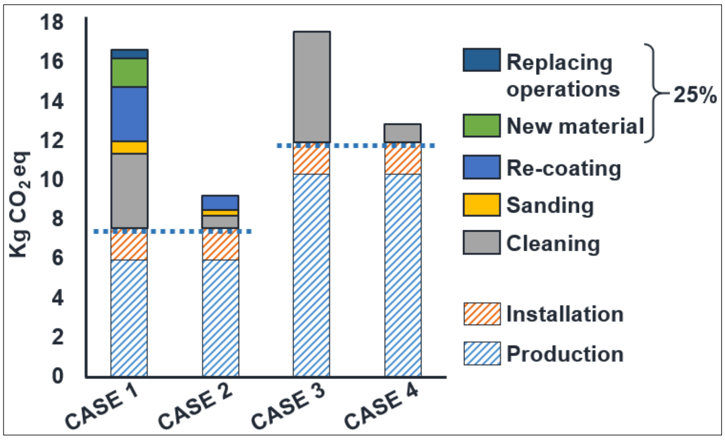

Figure 2: Environmental impact of production, installation and maintenance of 1 m^2 of façade made with untreated wood (case 1 and case 2) and chemically modified wood (case 3 and case 4) in high maintenance scenario (case 1 and case 3) and low maintenance scenario (case 2 and case 4).

For high frequency and intensity of maintenance, the total environmental impact of the natural wood façade and that of the chemically modified wood façade are comparable. In fact, the lower impact of the production of natural wood in comparison to the chemically modified wood is compensated by the higher impact of the maintenance operations for natural wood façade. However, in the mild climate, the natural wood has sensitively lower impact than chemically modified wood. The proposed system for interactive LCA is suitable for every possible combination of climate, material, design and customer aesthetical standard. Finally, in Table 2 we present the selection of the end-of-life scenario.

Table 2: End-of-life (EOL) features and their weights based on environmental impact. The total score indicates the environmental friendliness for each end-of-life option.

	Allow re-use	**Require additives**	**Reuse without processing**	**Reuse with processing**	**High energy**	**Low energy**	**Energy recovery**	**No energy recovery**	
Weights for EOL feature	**10**	**-5**	**7**	**3**	**-5**	**-1**	**5**	**-7**	**Total score**
Landfilling	0	0	1	0,1	0	1	0	0,9	**0**
Composting	0	0	0,1	0,9	0,1	0,9	0,2	0,2	**2**
Liquefaction	0,8	1	0	1	1	0	0,7	0,2	**3**
Fermentation	0,2	0	0,1	0,5	0,1	0,9	0,8	0,2	**5**
Anaerobic digestion	0,2	0	0,2	0,5	0,2	1	0,8	0,2	**6**
Combustion	0	0	0,1	0,9	0,1	1	1	0	**7**
Incineration	0	0	0,1	0,9	0,1	1	1	0	**7**
Pelletizing	0,4	0	0	1	0,9	0	1	0	**8**
Gasification	0,2	0	0,1	0,9	0,2	1	1	0	**8**
Pyrolysis	0,2	0	0,1	0,9	0,2	1	1	0	**8**

	Allow re-use	**Require additives**	**Reuse without processing**	**Reuse with processing**	**High energy**	**Low energy**	**Energy recovery**	**No energy recovery**	
Animal bedding	0,5	0	0	1	0,1	0,9	0,5	0,1	**8**
Panel manufacturing	0,9	0,5	0,2	0,8	0,8	0,2	1	0,1	**10**
Fungal conversion	0,7	0	0,8	0,4	0,1	0,9	0,4	0,2	**13**
Insect conversion	0,7	0	0,6	0,8	0,2	0,9	0,5	0,1	**14**
Re-use in solid products	1	0	1	0,1	0,1	1	1	0,1	**20**

CONCLUSIONS

In conclusions, the interactive LCA system that we propose allows rational choice of material and maintenance operation during service life. In fact, based on the location it will be possible to forecast a realistic maintenance plan, which will be customized according to the aesthetical expectation of the user.

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Raman spectral imaging of chemically modified Scots pine

Carmen-Mihaela Popescu[1], Lauri Rautkari[2], Michael Altgen[2], Tiina Belt[2],
Mikko Mäkelä[2]

[1]Petru Poni Institute of Macromolecular Chemistry of Romanian Academy, Iasi, Romania
[email: mihapop@icmpp.ro)]
[2]Department of Bioproducts and Biosystems, School of Chemical Engineering, Aalto University, P.O. Box
16300, FI-00076 Aalto [email: lauri.rautkari@aalto.fi, michael.altgen@aalto.fi, tiina.belt@aalto.fi,
mikko.makela@aalto.fi]

Keywords: Raman imaging, pine wood, chemical modification, anhydrides

ABSTRACT

Chemical modifications are helpful to improve some of the wood properties, like its dimensional stability, decay resistance and water sorption. During the modification, wood undergoes transformations depending on the chemical used, applied parameters and material properties. There are still important aspects which have not been fully elucidated concerning the chemical modification of wood and a better evaluation of these transformations will help understanding the enhancement of the materials properties and will promote the development of more durable products. The aim of this study is to get spatial and spectral information about the chemically modified Scots pine sapwood with different anhydrides. This will provide the degree of penetration of the chemicals in the wood cell wall. In order to determine this, the Raman spectral imaging technique and chemometric methods (e.g. Principal Component Analysis - PCA) were used. The structural features of unmodified and chemically modified Scots pine wood were evaluated by comparing the spectra recorded before and after the treatments and analysing the modification of the bands intensities. Further, on the basis of the acquired Raman imaging data set is possible to determine the distribution of chemical components in various wood cell wall layers. Therefore, PCA was employed to reduce the number of variables in a huge data set in the condition of retaining as much as possible of the variation present in the Raman spectral data set.

INTRODUCTION

Wood is an important natural material, with many technical advantages, such as: high specific stiffness and strength, low processing energy, high toughness, renewability, aesthetic properties, etc. However, despite these positive benefits, wood present some disadvantages: dimensional instability in a changing moisture environment and susceptibility to fungal decay. A way to improve these disadvantages is to use different treatments, *i.e*. thermal or chemical (Hill 2006).

Chemical treatment of wood involves the covalently bonding of chemical moieties to the wood cell wall polymers (Marfo *et al*. 2017, Kumar *et al*. 2018, Ozmen *et al*. 2006, Hill, 2006, Mantanis 2017). It is a method known to improve the dimensional stability, decay resistance, water sorption of wood and also the mechanical properties (Mai and Militz 2004).

As a result of this modification method, the hydroxyl groups in the cell wall are substituted partially and the cell wall of the wood is bulked with the bonded chemicals. The substitution of the hydroxyl groups reduces the number of primary sorption sites (which are generally assumed to be the OH groups); while the bulking reduces the volume in the wood cell wall which is available to water molecules (Popescu *et al*. 2014).

The most common chemical modification process involved reaction with anhydrides. Although in literature can be found many different anhydrides used, acetylation using acetic anhydride is the most studied and is also produced commercially (Mantanis 2017). The chemically treated wood it is often characterized by different spectral methods (mid-infrared, near infrared or Raman spectroscopies), in order to identify the structural modifications which may appear during the applied treatment.

In addition to infrared spectroscopy, Raman spectroscopy proved to be a useful method for the characterization of different materials, and their structural changes which appear after different treatments (Lavine *et al*. 2001, Agarwal and Ralph 1997). Coupling it with the microscopy, makes it possible to acquire information concerning the molecular structure and composition in a close to native state (Gierlinger *et al*. 2010) and to study changes in chemistry and microfibril orientation in cell wall layers, providing observation of the molecular and structural distribution at a specific point with high spatial resolution (Belt *et al*. 2017, Miyafuji *et al*. 2017). During recent decades, micro-Raman spectroscopy has been applied to investigate different natural cellulosic plant fibres and analyse the molecular changes during mechanical processing, tensile deformation, and chemical treatments (Miyafuji *et al*. 2017, Belt *et al*. 2017, Agarwal 2006, Gierlinger and Schwanninger 2007, Gierlinger *et al*. 2010). The functional characteristics of the cell walls depend on their polymeric composition and on their architecture at scales from a few nanometres to several microns (Pedersen *et al*. 2015, Gierlinger *et al*. 2010).

In this worked we aimed to get information regarding the spatial distribution and spectral information about the chemically modified Scots pine sapwood with three different anhydrides (acetic, propionic and butyric anhydrides). This will provide the degree of penetration of the chemicals in the wood cell wall. In order to determine this, the Raman spectral imaging technique and chemometric methods (*e.g*. Principal Component Analysis - PCA) were used.

EXPERIMENTAL

Materials

Scots pine sapwood samples (20 × 20 × 10 mm) were chemically modified with three different anhydrides: acetic anhydride (AC), propionic anhydride (PR) and butyric anhydride (BU), in order to get a series of different structures. The samples were vacuum-impregnated with neat pyridine and then heated to 100 °C in pyridine (1 h incubation) before the treatment in a 1 M solution of AC, PR or BU in pyridine at 100 °C for 2.5 h under reflux. Non-reacted chemicals were removed by acetone extraction in a Soxhlet apparatus. The WPG of the traded samples was of about 10% for AC and about 11% for PR and BU treatments.

Raman imaging

Raman images were acquired using a WITec alpha 300 R Raman microscope equipped with a 532 nm frequency doubled Nd:YAG laser, a 100 x immersion oil objective (NA = 1.25), and a DU970-BV EMCCD camera behind a 600 lines/mm grating. The size of each image was 35 µm x 35 µm, with 175 lines per image and 175 points per line. An integration time of 0.3 s was used. Cross-sections (20 µm in thickness) were cut from the ends of the sticks with a rotary microtome, after which the cross-sections were placed on objective slides with a few drops of water, covered with cover slips and edge sealed with nail polish.

RESULTS AND DISCUSSION

Raman spectra of the reference and chemically modified Scots pine wood samples are presented in Figure 1.

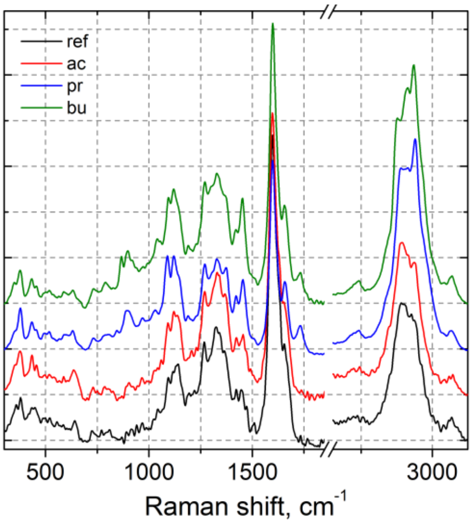
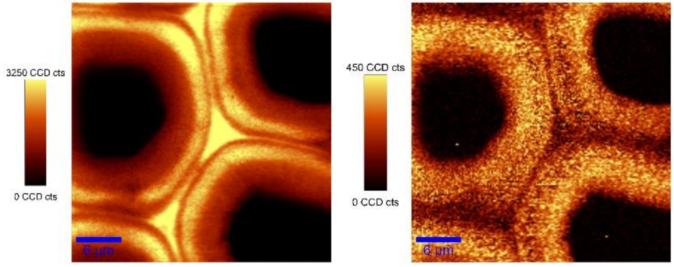


Figure 1. Raman spectra of the reference and chemically treated samples (latewood)

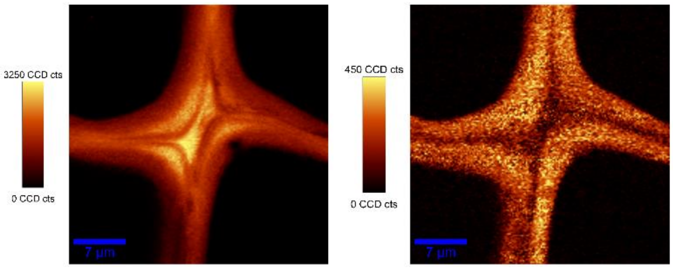
In the reference sample spectrum, due to its multicomponent nature, is characterized by broad overlapping bands. The main features in the wood Raman spectra arise from cellulose and lignin, whereas the hemicelluloses have been found to contribute less (Gierlinger *et al*. 2006). As can be observed from the spectrum of the reference wood sample, the spectral region between 2760–3150 cm^{-1} is assigned to C-H stretching vibration in lignin and carbohydrates. Further, in the region between 1520–1700 cm^{-1} are two bands located at 1603 and 1677 cm^{-1} which are assigned to aromatic ring symmetric stretching vibration in lignin. In addition, the band from 1124 cm^{-1} is assigned o stretching vibration of C-O-C linkages of carbohydrates. At lower wavenumber, between 300 and 480 cm^{-1}, the spectrum presents the bands assigned to stretching vibration of cellulose (Belt *et al*. 2017, Gierlinger and Schwanninger 2007, Zhang *et al*. 2015).

Further, the spectra of treated samples present modifications especially in the 2760–3150 cm^{-1} and 1000–1750 cm^{-1} regions. There is an increase of intensity and shifting of the bands maxima located in these regions with the type of treatment used.

In Raman imaging a large number of Raman spectra are collected in order to build a map with every pixel consisting in a spectrum. Figure 2 represent the two-dimensional Raman imaging maps of the latewood and earlywood for the reference sample calculated by integrating the areas of the aromatic lignin bands (1580-1620 cm^{-1}) (Figure 2a and c) and cellulose bands (340-390 cm^{-1}) (Figures b and d).

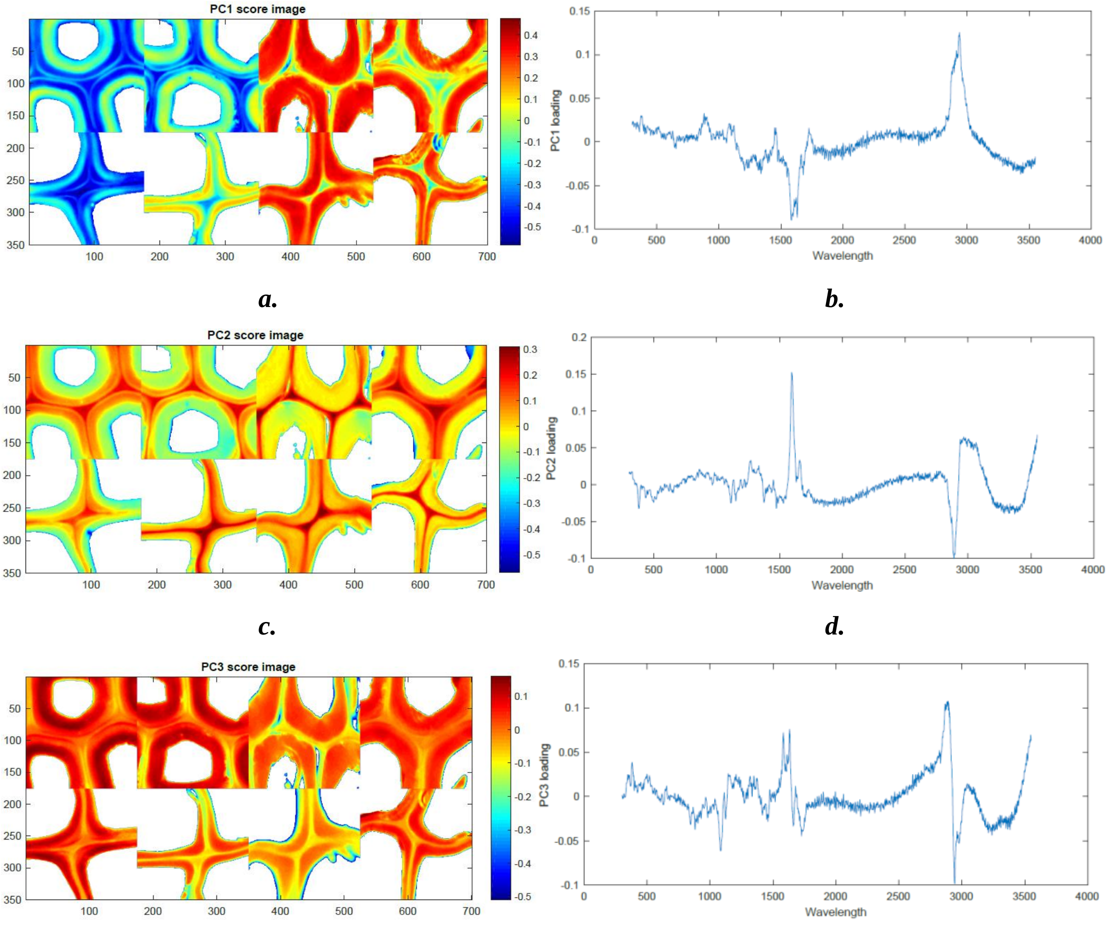


a. ***b.***



c. *d.*

Figure 2. Raman images of a cross-section of Scots pine reference sample latewood (a, b) and earlywood (c, d) by integrating over different wavenumber areas. Intensity of aromatic lignin band (1580-1620 cm^{-1}) (a and c) and the intensity of cellulose band (340-390 cm^{-1}) (b and d)



a. *b.*

c. *d.*

e. *f.*

Figure 3. PC scores images and loadings for the reference and treated wood samples

The key information included in Raman spectra concerning the relationships among analytes is usually distributed widely throughout the data set. By using multivariate methods of factor analysis, such as principal component analysis (PCA), it is possible to condense the essence of the information present in the spectral data into a very compact matrix representation (Zhang *et al*. 2015).

Considering a cumulative variance greater than 95%, the PC1, PC2, and PC3 components were selected to be taken into account for subsequent analysis, indicating that the selected PCs could reflect the original data very well. The PC score images and loadings are presented in Figure 3.

In the figures representing the score images (Figures 3a, 3c, and 3d), from left to right there are the untreated, acetylated, propionylated and butyrated wood samples for both regions latewood and earlywood. The loading plots indicate that PC1 present positive values for the bands assigned to chemical treatment, PC2 present positive values of the bands assigned to lignin, while PC3 for the bands assigned to cellulose.

CONCLUSIONS

Raman spectroscopy gives valuable information considering the structural modifications appearing after the chemical treatments applied to Scots pine wood. Further by combining it with microscopy it is possible to evaluate the molecular and structural distribution of the components in the wooden material and also to identify the degree of penetration of the chemicals in the wood cell wall. Further, PCA reduced the number of variables in a huge data set in the condition of retaining as much as possible of the variation present in the Raman spectral data set. PC scores and loadings gave clear differentiation between lignin, cellulose and chemical treatment.

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Changes in longitudinal modulus of elasticity of Douglas-fir during low temperature thermal treatment

Dan Ridley-Ellis[1] and Carmen-Mihaela Popescu[2]

[1] Edinburgh Napier University, UK [email: d.ridleyellis@napier.ac.uk)]
[2] Petru Poni" Institute of Macromolecular Chemistry of Romanian Academy, Iasi, Romania
[email: mihapop@icmpp.ro)]

Keywords: acoustic ndt, infrared spectroscopy, *Pseudotsuga menziesii*, resonance, stiffness

ABSTRACT

The change, during low temperature thermal treatment in air, of modulus of elasticity parallel to grain of Douglas-fir (*Pseudotsuga menziesii*) was monitored by the impulse excitation technique for temperatures of 110, 120, 130 and 140 °C. We combined these measurements with infrared (FT-IR) spectroscopy in an attempt to link the gradual loss in stiffness to changes in microstructure throughout 130 days of cumulative treatment. On a periodic basis we measured the stiffness by impact excitation in the minor axis flexural resonance mode. At the end of the treatment, the oven dry mass loss ranged from 1.6% at 110 °C to 13% at 140 °C and oven dry stiffness loss ranged from 4% at 110 °C to 29% at 140 °C. Further, in order to identify what structural changes influence the modifications in the stiffness, we used infrared spectroscopy on samples cut from the same original batch of timber. The spectra indicated modifications taking place for the amorphous polymers. More detailed information was given by chemometric methods, such as principal component analysis (PCA).

INTRODUCTION

Wood is an important material all over the world since ancient times. It is used in many applications in construction, furniture, and different practical or art objects. Wood is a natural material, which mainly consists of cellulose, hemicelluloses and lignin, and to some extent, depending on the species, with extractives, waxes and/or resins. During its service-life, wood experiences different transformations on its properties by a consequence of physical and chemical changes occurring in its structure due to the surrounding environmental and/or biological factors. Among environmental factors, temperature, humidity and UV radiation, and especially their variations, are the most aggressive ones and need to be considered during the wood service-life. Each of these factors act in different ways on the wood structure, inducing different modifications. Knowing the mechanisms of each deterioration type, and how these influence the wood structure and properties are key factors for conservation and bringing longevity to wood structures and objects.

Studies on wood thermal modification process have been conducted since the early 1950s with the aim to enhance the durability and moisture stability of wood. Generally, short period thermal treatments performed between 160 and 260 ^{o}C are used to improve some of the wood properties, lower temperatures inducing small changes in the wooden material properties, while higher temperatures induce strong degradation of the substrate (Hill 2006). Duration of treatment is also very important as the changes occurring in wooden structure under thermal treatments are also proportional to the period of the treatment. This study shows that even at temperatures similar to those used for industrial softwood kiln drying, and scientific gravimetric moisture content measurement, there are gradual and continuous degradation processes at work.

Dynamic tests based on resonance have often been applied successfully as a non-destructive evaluation technique in order to analyse, among other elastic and viscoelastic properties, the dynamic modulus of elasticity and quality factor of small, clear wood specimens at laboratory scale (Straže *et al*. 2015, Ridley-Ellis *et al*. 2018) and on sawn timber in industrial production.

Infrared spectroscopy is one of the most efficient characterization methods to identify the modifications appearing in the wood structure during heating. This technique proved to be an efficient tool to identify small modifications in the wood structure appearing during different thermal treatments (i.e. Tjeerdsma and Militz 2005, González-Penã and Hale 2011, Popescu *et al*. 2013, Sikora *et al*. 2018), decay (i.e. Ferraz *et al*. 2000, Popescu *et al*. 2010, Popescu *et al*. 2016) or photodegradation (i.e. Popescu *et al*. 2011, Tolvaj *et al*. 2016). Moreover, due to the use of small amount of sample and little or no processing this technique is also considered non-destructive.

The purpose of this study was to evaluate the mechanical properties and structural changes occurring in wood during thermal treatment in mild temperature conditions for periods up to 130 days using acoustic measurements and infrared spectroscopy.

MATERIALS AND METHODS

For this study we used a set of four matched clear, heartwood specimens of Douglas-fir (*Pseudotsuga menziesii* (Mirb.) Franco.) (PSMN) with nominal dimension 70 mm (radial), 18 mm (tangential) and 300 mm (longitudinal) in an oven for each of the four temperatures. The samples were heated for 130 days of cumulative treatment time, at 110, 120, 130 and 140 °C. The timber came from a common source, and all the matched samples were cut from the same plank. The original density of the timber was 589 kg/m^3 (coefficient of variation 2%) at 12% moisture content, and the original dynamic modulus of elasticity (MoE) was 15.6 kN/mm^2 (CoV 6%).

On a periodic basis the samples were removed from the oven, weighed hot and then allowed to cool in normal indoor conditions. After that, they were re-weighed, dimensions measured and their modulus of elasticity by impact excitation in the minor axis flexural resonance mode was assessed. Before returning to the oven, the samples were re-weighed. The measurement of oven dry weight and cold weight permitted calculation of moisture content at the time of measurement (mean 0.23%).

The induced vibration response for the studied samples was recorded with a USB computer microphone at 48 kHz and 16 bit depth and analysed with open source R software (R Core Team, 2018) and algorithms for enhanced precision, as described in Ridley-Ellis *et al*. 2018 (and http://blogs.napier.ac.uk/cwst/iet/). About 20 hits were made on each specimen at each measurement point, for which the standard deviation of measured frequency was about 0.2 Hz. The calculation of dynamic MoE used the average cold mass before and after measurement, a smoothed trend in dimension change, and the assumption that shear modulus is one sixteenth of the MoE.

Infrared spectra of the studied samples were recorded in ATR (attenuated total reflection) mode on a Bruker ALPHA FT-IR spectrometer equipped with a diamond cell. The resolution of the spectra was of 4 cm^{-1}. Five recordings for each sample has been made, and the media between them was retained for further analysis. Processing of the spectra was performed using the OPUS 7.5 software. Principal component analysis (PCA) was performed by using the ChemoSpec package (Hanson 2017) in R software.

RESULTS AND DISCUSSION

The mass loss values during the treatment are presented in Figure 1. As can be seen, the wooden samples underwent a linear trend of increasing mass loss with increasing the time of exposure to the thermal treatment, recording at the end of the treatment period a reduction of the weight of 1.6% (for the samples treated at 110 °C), 2.6% (at 120 °C), 5.6% (at 130 °C) and 13% (at 140 °C).

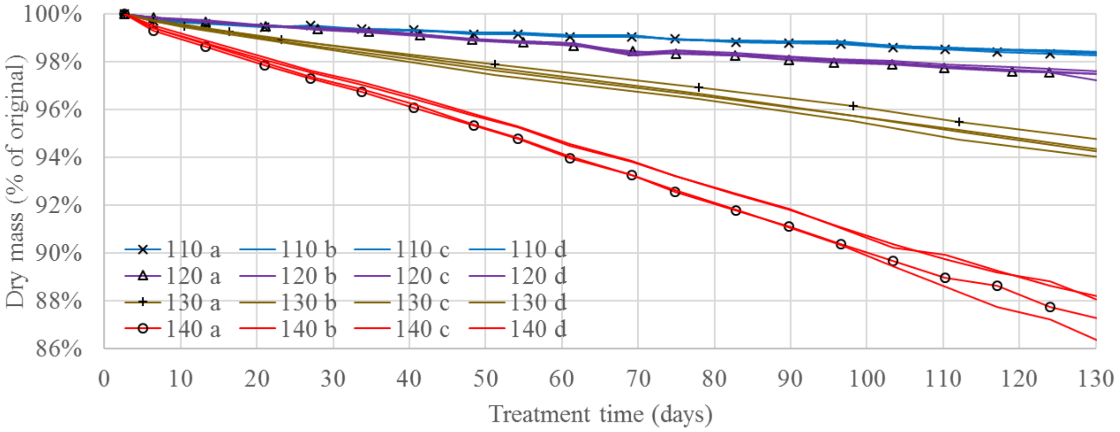

Figure 1: Change in dry mass during treatment (as % of original dry mass)

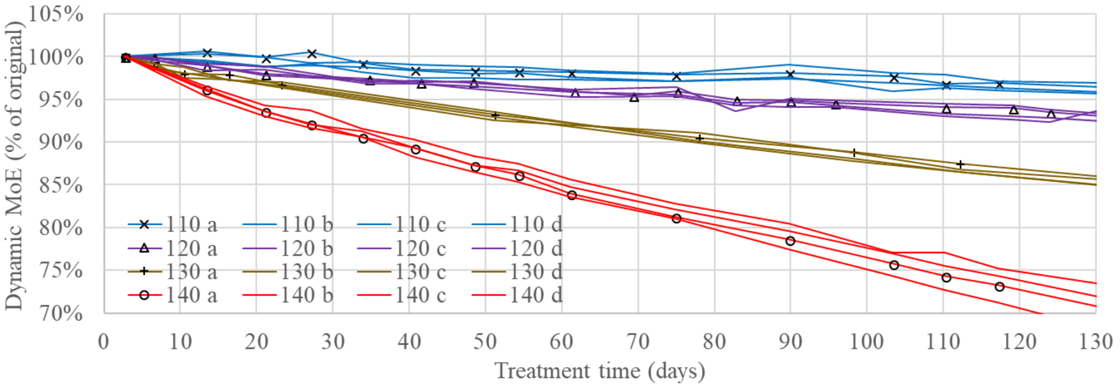

Figure 2: Change in dynamic modulus of elasticity during treatment (as % of original dry value)

The effect of the modification induced by the temperature on the wood stiffness was clear, the MoE percentage values decreased linearly with the increase of the treatment time (Figure 2). Similarly with the mass loss the highest rates of loss were recorded for the samples treated at 140 °C.

The rates of mass loss and stiffness loss, and dimensional change, are listed in Table 1 (length did not change measurably). The rates for both mass loss and MoE loss increase exponentially with temperature in this range (Figure 3). At 140 °C the rate of percent MoE loss is 2.2 times the rate of percent mass loss, and at 120 °C it is 2.7 times. The trend for this ratio appears it may be different at 110 °C than for the higher temperatures, but there is also increased variation between the individual specimens (perhaps due to the smaller changes being more obscured by measurement error).

Table 1: Rate of change in properties during treatment

Temperature (°C)	Radial dim.	Tangential dim.	Dry mass	Dynamic MoE
	[change as a % of original measurement / day][a]			
110 ± 2.5	-0.002% (0.49)	-0.000% (0.02)	-0.011% (0.99)	-0.029% (0.94)
120 ± 2.5	-0.005% (0.82)	-0.001% (0.06)	-0.019% (1.00)	-0.052% (0.95)
130 ± 2.5	-0.009% (0.95)	-0.008% (0.58)	-0.043% (1.00)	-0.111% (0.99)
140 ± 2.5	-0.016% (0.98)	-0.020% (0.96)	-0.096% (1.00)	-0.208% (0.99)

[a] *The coefficient of determination is given in parenthesis*

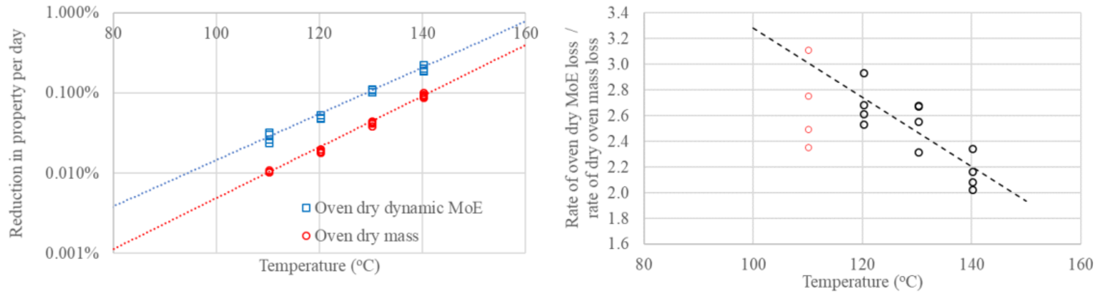

Figure 3: Percentage reduction in dry mass and stiffness per day (left) and the ratio of these rates (right) at different temperatures

Infrared spectra of the reference and treated wood samples at 140 °C (as an example) are presented in Figure 4. The spectra indicate typical bands of the wood material, with two main regions: 3700-2700 cm^{-1} assigned to OH and CH stretching vibrations and 1800-800 cm^{-1} assigned to different stretching and deformation vibrations of the functional groups from the wood structure.

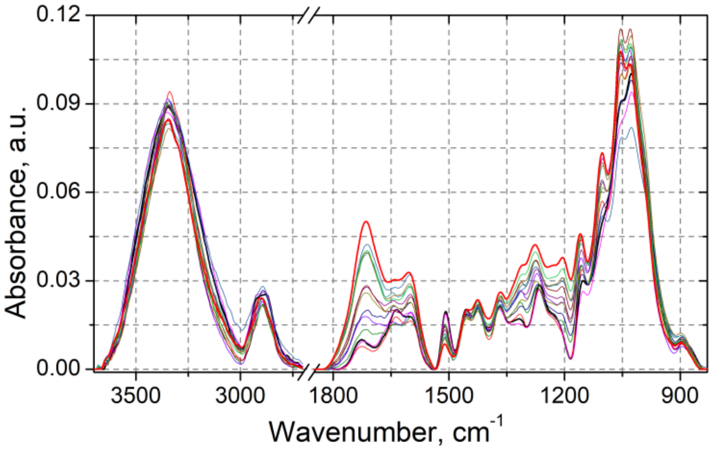

Figure 4: Infrared spectra of the reference and treated wood samples at 140 °C

During the thermal treatment some modifications can be evidenced, with higher variations recorded for the samples treated at 140 °C (as it was expected). Therefore, the bands from 1712 cm^{-1} (assigned to carbonyl and carboxyl groups stretching vibration), 1205 and 1159 cm^{-1} (assigned to C−O−C stretching mode of the pyranose ring especially from crystalline cellulose), 1102 and 1053 cm^{-1} (assigned to C−O stretching vibration mainly from C(3)−O(3)H in cellulose) increased in intensity with the increase of the treatment time. The increase in intensity of the band from 1712 cm^{-1} indicate the formation of new carbonyl and carboxyl structures, while the increase of the other bands indicate a decrease of the amorphous polymer fraction from the wood structure, especially the hemicelluloses, but also lignin. The modification in the structure of lignin is also evidenced by modification of the intensity and position of the maximum with 5 cm^{-1} to higher wavenumbers of the band from 1507 cm^{-1} (assigned to C=C from the aromatic ring). Same modifications were observed for the spectra of the samples treated at the other temperatures, but to a lower extent.

Further, in order to get more detailed information, principal component analysis has been applied. It is known that this method gives detailed information regarding the differences which appear between the series of similar samples. The principal components scores clearly differentiate the samples groups according to temperature and time.

CONCLUSIONS

Douglas fir wood samples were exposed to four different temperatures (110, 120 130 and 140 ^{o}C) for a period of 130 days. Elastic properties and structural changes were evaluated by impact excitation and infrared spectroscopy. Mass and stiffness decreased linearly with the increase of the treatment time, showing no sign of slowing trend even for the 140 °C treatment. The rates increased exponentially with temperature (in this range) and at higher temperatures the rate of mass loss was higher compared to the rate of stiffness loss. This implies that not all of the mass loss is linked to reduction in stiffness. Infrared spectra indicate modification in the structure of the amorphous phase and formation of new carbonyl/carboxyl compounds.

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Investigation of the effect of moderate heat treatment on wood hygroscopicity by NMR relaxometry

Leila Rostom[1], Denis Courtier-Murias[2], Stéphane Rodts[3] and Sabine Caré[4]

[1]PhD Student, Laboratoire Navier, UMR 8205, Ecole des Ponts, IFSTTAR, CNRS, UPE, Marne-la-Vallée, France [email: leila.rostom@enpc.fr)]
[2]Researcher, Laboratoire Navier, UMR 8205, Ecole des Ponts, IFSTTAR, CNRS, UPE, Marne-la-Vallée, France [email: denis.courtier-murias@ifsttar.fr)]
[3]Researcher, Laboratoire Navier, UMR 8205, Ecole des Ponts, IFSTTAR, CNRS, UPE, Marne-la-Vallée, France [email: stephane.rodts@ifsttar.fr)]
[4]Researcher, Laboratoire Navier, UMR 8205, Ecole des Ponts, IFSTTAR, CNRS, UPE, Marne-la-Vallée, France [email: sabine.care@ifsttar.fr)]

Keywords: Hygro-mechanical properties, Moderate heat treatment, NMR, Physical aging, Wood.

ABSTRACT

This study aims to evaluate the effect of moderate heat treatment (at 120°C for 24 hours) on new and 350-year-old oak wood samples and to provide information, at the molecular scale, on bound water and on the interactions between water and wood polymers. Each sample, before and after heat treatment, was equilibrated for one week at 65 % relative humidity. 2D ^{1}H NMR relaxometry was used to investigate the changes at the scale of the wood's components as it allows to quantitatively measure two pools of bound water in the wood cell walls. NMR results suggest differences between these pools of bound water (one is more strongly associated to wood polymers than the other is) and that they should be associated to different wood polymers. Results show that heat treatment induces a more important modification of the strongly associated water pool (supposed to be in interaction with the glucuronoxylan-cellulose matrix). The other water pool (which is supposed to be essentially associated to lignin-xylan matrix) is less affected by heat treatment. These results could be explained either by a selective degradation of glucuronoxylan and cellulose matrix or by global changes on wood polymers that modify water accessibility. In addition, further investigations with ^{13}C NMR or IR could help to better understand these changes as they can directly observe wood polymers. These results show the ability of 2D NMR relaxomety to evaluate the effect of heat treatments at the molecular level.

INTRODUCTION

Wood, as an envelope or structural material, is a material of interest in the field of construction both for new buildings and for the question of renovation of old buildings. The built heritage shows that wood makes it possible to design buildings that are sustainable and healthy. In order, however, to estimate lifetimes or to propose methods of maintenance, it is necessary to continue the research efforts to understand the mechanisms of physical aging of wood and its hygro-mechanical properties at the scale of its constituents.

Aging is a complex phenomenon that modifies physical, chemical and mechanical properties of a polymeric based material, under the effect of its proper instability, environmental parameters or mechanical strain. As a natural and biodegradable resource, wood is mainly constituted of three biopolymers: cellulose, hemicellulose and lignin. These components can be vulnerable to environmental factors such as temperature, solar radiation, humidity, which can create degradation of wood's polymeric structure. Studies have shown a decrease of cellulosic material in old wood compared to new wood as well as a decrease in lignin content (Kránitz *et* *al.* 2016). Similarly, natural aging or artificial aging (through heat treatment) of wood shows a decrease in the Equilibrium Moisture Content (EMC) and an improved dimensional stability of wood due to a decrease in adsorption sites in the polymers chains of the wood cell walls (Murata *et al*. 2013). Numerous studies have been conducted to develop industrial processes varying in terms of temperature (generally at high temperature between 160°C and 280°C), duration and vector (gas, water vapour, oil…) (Esteves and Pereira 2008). The higher the temperature of treatment (and the longer the time of treatment) the greater the dimensional stability of wood (Inari *et al*., 2009; Chaouch 2011; Endo *et al*. 2016). These processes allow using low durability timbers by making them more resistant to fungi attacks and thus improving their decay resistance. However, these treatments' intensity does considerably weaken the mechanical properties of timbers such as bending and compression strengths, stiffness and shear strength (Candelier 2016). Thermal treatments at lower temperature need to be more investigated in order to improve the decay resistance as well as the mechanical properties of timber, and to simulate natural aging as old wood is supposed to be more 'stable' than new wood.

The use of proton Nuclear Magnetic Resonance (^{1}H NMR) relaxometry to detect bound water in the wood's cell walls is gaining popularity in the research field as it is a non-invasive and non-destructive method allowing to study the same material subjected to different loadings. Here, we investigate the state of water adsorbed on the wood's cell walls through ^{1}H low-field (LF) NMR relaxometry. This technique has shown good accuracy in terms of water identification and quantification in the wood cell walls and lumens (Araujo *et al*. 1994). This has been mainly done by measuring T_2 relaxation times. Recent studies (Bonnet *et al*. 2017) that used two-dimensional (2D) T_1-T_2 correlation spectra have shown the presence of two bound water components (B and C in Fig. 1), in the hygroscopic range. The distributions obtained through 2D T_1-T_2 ^{1}H NMR correlate information about the longitudinal relaxation time T_1 (spin-lattice interactions) and the transversal relation time T_2 (spin-spin interactions) which enables a better splitting than 1D NMR of the water components. The relaxation times T_1 and T_2 are dependent on the affinity of protons with their local environment, that is to say: size of the molecules they are bonded to, affinity with these molecules and pore size. In general, protons having relatively short T_2 relaxation times, have a relative high interaction with the local chemical composition, and thus will be in relatively small pores. In wood studies, this water pool corresponds to bond water in the wood's cell walls. Whereas water that has higher T_2 relaxation times is less confined and is more likely to correspond to free water in lumens. In addition, T_1/T_2 ratios are characteristic of the mobility and confinement of H atoms and greatly help spectrum interpretation. Depending on the value of these ratios, water can be assigned to unconfined water, mobile water in a free or adsorbed state and bonded immobile water molecules and solid macromolecules. Ratios lower than one are physically not permitted (Bonnet *et al*. 2017). This technique is the sole tool capable to observe two different types of bound water in wood. Thus, 2D ^{1}H NMR correlation spectra is a great method that can provide an insight on the water environment inside the lingo-cellulosic matter and the influence of the microstructure and chemical composition on the hydrogen signal observed.

The purpose of this study is to evaluate the correlation between water loss and the behaviour of the cell wall structure before and after a moderate heat treatment. Therefore, 2D ^{1}H NMR relaxometry is used to identify the two different types of bound water in the wood cell walls and permits to correlate the changes observed in moisture content (for each type of bound water individually) with the physical and chemical changes that may have occurred. A parallel objective is to compare these changes between old and new wood samples.

EXPERIMENTAL

Experimental protocol

The experiments were carried out with new and old oak wood samples. The old oak wood was provided by Atelier Perrault, and comes from a wooden door's frame of an old building of the 17th century in Saint Georges street in Rennes, France. The new wood was provided from a sawmill located in the North of France. Density of specimens was measured and is 640 kg.m^{-3} for new oak wood and 480 kg.m^{-3} for old oak wood. Small wood specimens of 1cm^3 were prepared using a band saw. They were all clear from visible defects and subjected to a common cycle of adsorption-desorption in order to equalize their hydric history. All the experiments were carried out on an adsorption cycle (starting from 2% relative humidity (RH)) in order to avoid the influence of the hysteresis in the observed phenomena.

Thermal treatments were conducted in an oven at a temperature of 120°C (393.15K) for 24 hours. Prior to the heat treatment, the specimens were conditioned at 65% RH and investigated through 2D ^{1}H NMR at equilibrium moisture content (EMC) at 20°C. After the heat treatment, the specimens were again conditioned at 65% RH, 20°C before the second NMR analysis. Mass and dimensions were measured before and after treatment in order to assess the mass loss and the change in dimensions as this provides information on the stability of the wood following the heat treatment. In this paper, only NMR results of specimens are given. Three specimens were considered for each case to take into account the variability of wood material and to test the reproducibility and the repeatability of the used method.

2D ^{1}H NMR method

The sample was inserted in a 18mm NMR tube with a maximum height of 10mm imposed to the samples for an optimum operating performance. The RH is controlled with a saturated salt solution during the NMR measurement (Bonnet *et al*. 2017).The device used is a BRUKER MINISPEC MQ20 spectrometer which operates at 0.5 T, corresponding to a resonance frequency of 20 MHz for ^{1}H. The Inversion Recovery (IR) sequence coupled with the Carr-Purcell-Meiboom-Gill (CPMG) sequence (Hahn 1949; Carr and Purcell 1954) is usually used to measure the longitudinal (T_1) and the transversal (T_2) evolutions. NMR parameters can be found in Bonnet *et al.* (2017)

RESULTS AND DISCUSSION

^{1}H T_1-T_2 NMR correlation spectra

The T_1-T_2 NMR correlation spectra (Figure 1) show the signal of hydrogen atoms detected before and after heat treatment for both new and old oak wood. The peak designated as D corresponds to hydrogen atoms of wood molecules. Indeed, the short T_2 and the long T_1 relaxation time gives a high T_1/T_2 ratio, which reveals a little mobility of atoms and is the signature of relatively rigid molecules (Bonnet *et al*. 2017). A higher T_2 relaxation time is observed for peaks B and C, which also show a lower T_1/T_2 ratio than that of the peak D, revealing a greater mobility of those hydrogen atoms. Thus, they are attributed to bound water in the cell wall's polymers. Moreover, the T_1 relaxation time for peak B is different from that of the peak C revealing that bound water is located in two specific regions in the cell walls. Peak B has a higher T_1/T_2 ratio than peak C indicating a more restricted molecular motion and suggesting stronger interactions with wood molecules. In Bonnet et al. 2017, the two bound water components were assigned, for Douglas fir, as follows: the strongly bound water (B-water) may be located in the macrofibrils (cellulose-glucomannan matrix) - and the weakly bound water (C-water) in the lignin-xylan matrix. This hypothesis could also be used to interpret our results. However, the percentage and the composition of hemicelluloses differ between hardwoods and softwoods. Hardwoods contain mainly glucuronoxylan and low amount of glucomannan. Moreover, xylan units are strongly acetylated compared to softwoods which could lead to higher kinetic of thermo-degradation since the deacetylation of hemicelluloses causes liberation of acetic acid, which catalyzes depolymerisation of the less ordered carbohydrates (hemicelluloses and amorphous cellulose) (Chaouch *et al.* 2010). The T_1-T_2 correlation spectra reveal a decrease of the T_1/T_2 ratio after a heat treatment, which means that hydrogen atoms are a little more confined and more strongly bonded to the polymers. The phenomenon relying behind this observation is not yet understood and further measurements could help to explain it.

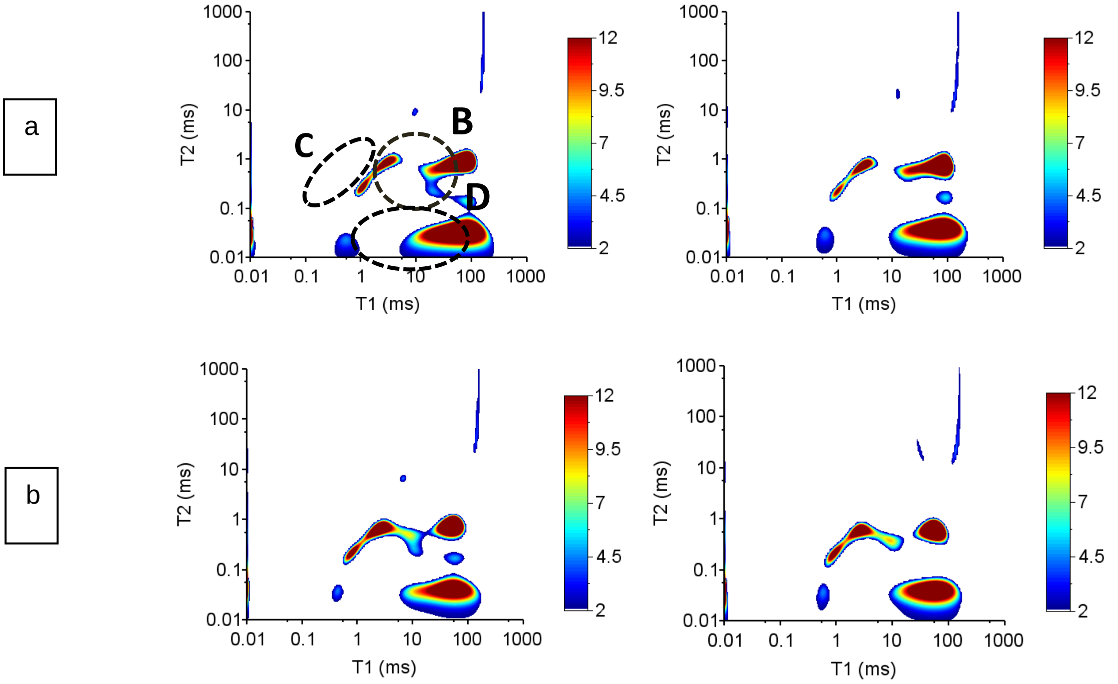

Figure 4: ***T_1-T_2 correlation spectra of new (a) and old (b) oak wood for samples conditioned at 65% RH. Left: Before heat treatment. Right: After heat treatment.***

Moisture content

The moisture content was calculated by converting the peak areas of B and C into quantity of bound water using a standard curve and is defined as the ratio between the mass of bound water and the mass of dry wood (determined at 2%RH). Results given in Table 1 show a clear reduction in total moisture content after heat treatment and reconditioning at 65% RH for both old and new oak wood, accompanied with mass loss. This decrease of water content is in accordance with the decrease of the swelling strains between 2% RH and 65% RH. Moreover, T_1T_2 NMR experiments allow us to measure the effect of heat treatment for the two types of adsorbed water. Moreover, results given in Table 1 show a higher percentage of water loss in the B-water compartment than in the C-water compartment for both oak wood materials. The reason of this selective loss of water adsorption is not known yet. As suggested by the interpretation of T_1T_2 correlation spectra (Bonnet et al 2017), this selective loss of water could be due to modifications occurring preferentially in the macrofibrils and due to a loss of adsorption sites. However, according to Kollmann and Fengel (1965) in Esteves and Pereira (2008) wood degradation begins only at 130-150°C for oak wood. Thus, by heating at 120°C, there should not be any degradation of polymers. Another hypothesis could be that the accessibility of the B-water compartment's polymers is restricted due to other changes in the cell wall, such as structural modifications due to extractive modifications during heat treatment. ^{13}C NMR could be of good use here to determine the modifications that occurred during the heat treatment.

Table 1: Total moisture content (B+C), B-water and C-water content before and after heat treatment at 120°C for 24 hours for samples conditioned at 65% RH.

Sample		**B+C (%)**	**B (%)**	**C (%)**
New oak wood	Before treatment	11.9	9.2	2.7
	After treatment	10.4	7.9	2.5
Old oak wood	Before treatment	11.3	7.7	3.6
	After treatment	10.1	6.8	3.3

CONCLUSIONS

This study shows the potential of the ^{1}H NMR correlation spectra to study heat treatments of wood, which helps us to quantify two types of water adsorbed in the wood cell walls. A heat treatment was performed on new and old oak wood samples at 120°C for 24 hours. Results show a decrease in moisture content after the heat treatment and more precisely a higher loss in the B-water component. The polymers associated to this component might not have undergone modifications because of the low temperature of heating and the extractives present in wood could be the cause of the structural modifications that occurred. Thus, we hypothesize that the accessibility of the B-water compartment's polymers is restricted due to other structural modifications in the cell wall. In addition, these observations could be completed with ^{13}C NMR or IR investigation to determine the changes that occurred in wood polymers more precisely. A recovery test could be performed as well as a complete isotherm in order to determine the difference in evolution of EMC intake (and dimensional change) between the old and the new wood.

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Effect of wood modification and weathering progress on the radiation emissivity

Paolo Grossi[1], Jakub Sandak[2,3,4], Marta Petrillo[5] and Anna Sandak [6]

[1]CNR-IVALSA, via Biasi 75, 30010 San Michele all'Adige, Italy [email: grossi@ivalsa.cnr.it]
[2]InnoRenew CoE, Livade 6, 6310 Izola, Slovenia [email: Jakub.Sandak@innorenew.eu]
[3]CNR-IVALSA, via Biasi 75, 30010 San Michele all'Adige, Italy [email: sandak@ivalsa.cnr.it]
[4]University of Primorska, Faculty of Mathematics, Natural Sciences and Information Technology, Glagoljaska 8, 6000 Koper, Slovenia
[5]CNR-IVALSA, via Biasi 75, 30010 San Michele all'Adige, Italy [email: petrillo@ivalsa.cnr.it]
[6]CNR-IVALSA, via Biasi 75, 30010 San Michele all'Adige, Italy [email: anna.sandak@ivalsa.cnr.it]

Keywords: emissivity, modified wood, thermography, thermal images, weathering, heat transfer

ABSTRACT

The research reported here is a part of the BIO4ever project, which aims to develop numerical models simulating performance of the bio-based cladding materials in relation to the exposure time or so-called "weather dose". The value of emissivity is one of the thermodynamic material constants, highly affecting heat transfer calculations. The lack of reliable emissivity data for several investigated materials was discovered during model's preparation, especially in a case of modified woods and coated samples. It was especially important since the emissivity is directly affecting the surface state/condition, and might change due to the weathering process. The overall objective of this research was therefore to determine actual emissivity coefficients for diverse cladding materials (various wood species and modification processes) in different ambient conditions (temperature).

The thermographic (radiometric) measurements were conducted with the thermal camera FLIR T200, covering a spectral range from 7.5 to 13 µm. Tests were carried out on preselected samples to highlight the differences between diverse materials. The emissivity coefficient was determined at different surface temperatures by conditioning samples in climatic chambers for a period of at least six hours. The emissivity values obtained experimentally were used for improvement of finite element method models of the solar irradiation and of the surface moisture content changes for all investigated bio-materials. Subsequently, simulation of the façade appearance implemented within BIO4ever project, considering simultaneously time of service, geographic location, local microclimate and intrinsic material characteristic, become more realistic and trustworthy.

INTRODUCTION

Infrared thermography is a non-destructive and non-contact testing method that is applied in building physics to evaluate structure's energetic performance (Barreira *et al*. 2016). The technology is especially interesting nowadays when infrared measuring instruments become portable and affordable, being reasonably accurate at the same time (Sandak and Sandak 2017). The emissivity (material property), is defined as an amount of electromagnetic energy radiated from the material's surface to that radiated from a blackbody. The emissivity is usually defined in two spectral bands, including solar (short wavelength λ <2.5µm) and ambient (long wavelength λ >2.5µm) ranges. The usual procedure of emissivity estimation bases on the measurements of a single sample conditioned to the thermodynamic equilibrium (heating or cooling) with the surrounding ambient (Pitarma *et al*. 2016). The main disadvantage of this procedure is relatively long time that elapses before the thermal image readings, especially when the difference of temperature between the sample and the ambient is high.

In alternative, the emissivity can be determined according to ASTM1933 standard, using a radiometer (IR camera, spot IR thermometer) with two complementary methods, namely "contact thermometer method" or "noncontact thermometer method". The first method requires a direct measurement of the target surface temperature through a contact thermometer. This measurement became the reference value used to manually adjust the settings of the radiometer (first iterative step). The material specific value of emissivity is properly adjusted when equal temperatures are determined by both reference thermometer and radiometer. The second method bases on an emissivity value correction by comparing instrument readings with these performed on reference material. It is important to assure that both, reference and characterized materials are at the thermal equilibrium. The reference temperature is determined with reference material, considering its known emissivity and specific boundary conditions. In the second step, the radiometer settings are adjusted to correct the apparent temperature according to the value of reference surface temperature. Both methods are considered to have a good precision and reproducibility.

The research reported here is a part of the BIO4ever project, which aims to develop numerical models simulating performance of the bio-based cladding materials in relation to the exposure time or so-called "weather dose". The emissivity is one of the thermodynamic material properties (constants) used for heat transfer calculations. The lack of real emissivity data for several investigated materials was discovered during FEM (finite element method) model's preparation, especially in a case of modified woods and coated samples. The motivation for this research was therefore to experimentally determine real emissivity coefficients for diverse cladding materials (various wood species and modification processes) in different ambient conditions (temperatures).

EXPERIMENTAL

Experimental samples

Twenty different cladding materials investigated within BIO4ever project were selected as experimental samples (Table 1). The set included natural, thermally modified, chemically modified, impregnated, coated, surface treated wood and bio-based composites.

Experimental set-up

The setup of experimental determination of emissivity coefficient is presented in Figure 1. A thermal IR camera (FLIR T200) with a 240×180 pixels resolution with a shutter time of 100ms was used to acquire the thermal images. The camera was fixed on a tripod and exposed in the front of a sample holder (made of polyester box), minimizing infrared reflections from surround. The spectral range of the IR camera covered 7.5 to 13µm. The measurable temperature range was from -20 to 350°C, with a producer declared accuracy of ±2%. The thermal sensitivity (smallest temperature difference measurable) at 30°C was <0.08°C. The vision angle of used lenses was 25° with a minimum focusable distance between the object and the camera of 0.4 m.

Table 1: Materials investigated within this research

Sample#	**Species**	**Material category (modification)**						
		natural	**composite**	**thermal**	**chemical**	**impregnated**	**surface**	**hybrid**
A1	larch	●						
A2	scots pine					●		
A3	bamboo	●						
A4	frake			●				
A5	acetylated fiberboard		●					
B1	spruce			●				
B2	bamboo	●						
B3	acetylated fiberboard		●					
B4	radiate pine						●	
B5	bamboo fiberboard		●					
C1	pine				●			
C2	spruce					●		
C3	WPC		●					
C4	larch						●	
C5	larch	●						
D1	spruce							●
D2	pine							●
D3	spruce						●	
D4	radiate pine				●			
D5	beech					●		

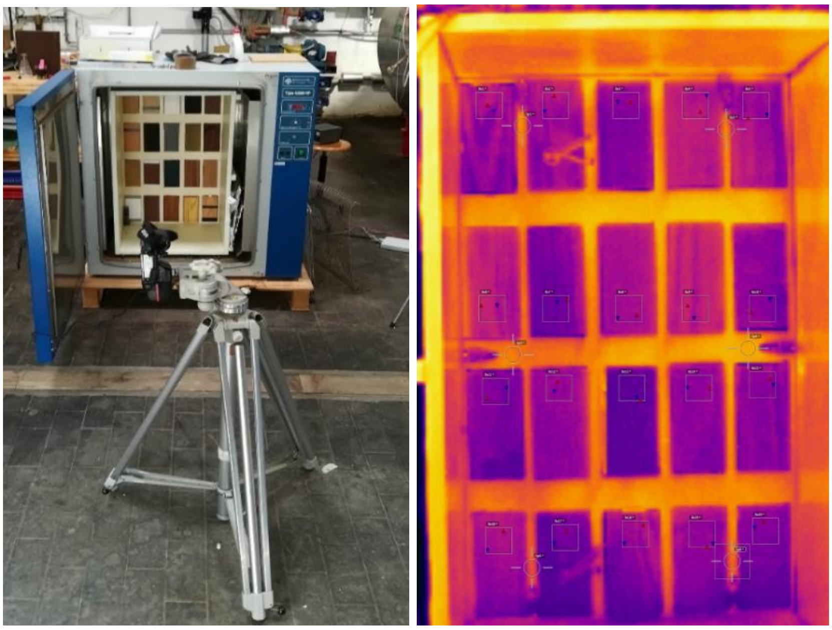

Figure 1: FLIR T200 thermal camera test setup (left), thermal image result of a test (right).

Calculations

The electrical signal recorded by the camera was transformed into a temperature value according to Equations 1, 2 and 3. The total radiation received by the camera (W_{tot}) can be expressed as the sum of the radiation emitted by the object (E_{obj}), radiation reflected by surroundings (E_{refl}) and the emission of the atmosphere (E_{at}).

$$W = E_{obj} + E_{refl} + E_{at} \qquad (1)$$

$$W_{tot} = \varepsilon_{obj} \cdot \sigma \cdot {T_{obj}}^4 \cdot \tau_{at} + \left(1 - \varepsilon_{obj}\right) \cdot \sigma \cdot {T_{refl}}^4 \cdot \tau_{at} + (1 - \tau_{at}) \cdot \sigma \ \cdot {T_{at}}^4 \qquad (2)$$

$$T_{obj} = \sqrt[4]{\frac{W_{tot} - \left(1 - \varepsilon_{obj}\right) \cdot \tau_{at} \cdot \sigma \cdot \left(T_{refl}\right)^4 - (1 - \tau_{at}) \cdot \sigma \cdot (T_{amb})^4}{\varepsilon_{obj} \cdot \tau_{atm} \cdot \sigma}} \qquad (3)$$

where; ε_{obj} is the target emissivity, T_{refl} is the reflected temperature, T_{amb} is the ambient temperature, T_{at} is the transmittance of the atmosphere, σ is the Stefan Boltzman constant.

The energy emission from the object and the reflected radiation detected by the sensor is reduced because the atmospheric air absorbs a part of the radiation. The effect of the atmosphere on the signal is compensated when setting of temperature (T_{amb}), considering also relative humidity of the air and distance between target and camera.

Testing procedure

The set of 20 samples was conditioned at different temperatures in two environments; low temperature (-2.5°C) in a refrigerator and the high temperature (35.0°C) in a laboratory oven. The reference temperatures in both climatic chambers were assessed with different thermometers. Six DHT22 sensors measuring temperature and relative humidity and two MLX9014 infrared thermometers were placed in diverse positions over the sample holder box. It was possible therefore to determine detailed temperature gradient (reference sample temperature) within the camber after sample conditioning. Signals from sensors were acquired with Arduino controller and post-processed on the PC. The software used for thermal images analysis was FLIR Reporter.

The raw thermometric image was acquired using value of emissivity $\varepsilon = 1.00$. The real value of ε was determined according to Equation 4 on the base of information collected by the thermal camera and temperature sensors.

$$\varepsilon_{obj} = \frac{{T_{obj,r}}^4 - {T_{amb}}^4}{{T_{obj}}^4 - {T_{amb}}^4} \qquad (4)$$

where. $T_{obj,r}$ - the sample surface temperature from the thermal image at $\varepsilon = 1.00$, T_{obj} - the reals surface temperature of conditioned samples measured by the nearest thermometer, T_{amb} - the temperature of the ambient measured close to the thermal camera.

RESULTS AND DISCUSSION

The summary of experimentally determined values of emissivity *ε* is presented in Table 2. Five independent tests were conducted at each ambient condition in order to improve statistical reliability of *ε* values computed. The variations within measurements were related to the limited accuracy of IR thermal camera as well as to the uncertainty of the reference temperatures of the evaluated samples surface. The latest temperature was measured as close as possible, but anyway not directly on the sample surface.

It is evident from the results obtained that the emissivity *ε* values are different for all cladding materials characterized. In the extreme cases the value of *ε* ranged from 0.84 (material A4 – thermally modified frake) to 0.96 (material C3 – wood-plastic composite).

Table 2: Emissivity ε of bio-based materials conditioned in diverse climatic conditions

Material	**temperature T_{amb} = -2.5°C**						**temperature T_{amb} = 35.0°C**					
	Test #1	**Test #2**	**Test #3**	**Test #4**	**Test #5**	**Mean**	**Test #1**	**Test #2**	**Test #3**	**Test #4**	**Test #5**	**Mean**
A1	0.90	0.92	0.93	0.94	0.91	**0.92**	0.92	0.91	0.95	0.92	0.89	**0.92**
A2	0.93	0.90	0.92	0.90	0.89	**0.91**	0.88	0.88	0.91	0.89	0.87	**0.89**
A3	0.93	0.92	0.93	0.91	0.91	**0.92**	0.90	0.90	0.93	0.93	0.89	**0.91**
A4	0.88	0.88	0.88	0.87	0.86	**0.87**	0.86	0.88	0.9	0.88	0.87	**0.88**
A5	0.89	0.91	0.91	0.89	0.88	**0.90**	0.88	0.93	0.92	0.89	0.89	**0.90**
B1	0.91	0.89	0.90	0.88	0.89	**0.89**	0.88	0.89	0.91	0.89	0.88	**0.89**
B2	0.96	0.95	0.95	0.94	0.93	**0.94**	0.92	0.93	0.95	0.93	0.91	**0.93**
B3	0.90	0.92	0.91	0.90	0.91	**0.91**	0.90	0.92	0.91	0.9	0.88	**0.90**
B4	0.89	0.90	0.91	0.89	0.90	**0.90**	0.90	0.92	0.89	0.88	0.89	**0.90**
B5	0.92	0.94	0.94	0.93	0.94	**0.94**	0.91	0.93	0.94	0.93	0.9	**0.92**
C1	0.95	0.93	0.94	0.92	0.93	**0.94**	0.92	0.92	0.94	0.93	0.89	**0.92**
C2	0.93	0.92	0.93	0.91	0.90	**0.92**	0.91	0.93	0.92	0.89	0.88	**0.91**
C3	0.97	0.97	0.95	0.96	0.96	**0.96**	0.94	0.92	0.95	0.95	0.92	**0.94**
C4	0.93	0.94	0.95	0.93	0.94	**0.94**	0.93	0.94	0.93	0.9	0.91	**0.92**
C5	-	0.94	0.94	0.93	0.94	**0.94**	0.91	0.93	0.91	0.91	0.9	**0.91**
D1	0.91	0.90	0.91	0.90	0.89	**0.90**	0.90	0.92	0.92	0.9	0.89	**0.91**
D2	0.97	0.95	0.93	0.94	0.93	**0.94**	0.92	0.92	0.94	0.93	0.91	**0.92**
D3	0.93	0.92	0.91	0.90	0.91	**0.91**	0.89	0.89	0.9	0.9	0.88	**0.89**
D4	0.89	0.90	0.90	0.90	0.88	**0.89**	0.89	0.89	0.9	0.89	0.88	**0.89**
D5	0.91	0.91	0.91	0.91	0.89	**0.91**	0.90	0.90	0.9	0.9	0.89	**0.90**

It has to be mentioned that IR camera detects infrared radiation emitted not only by the target object but also related to other sources of heat, such as neighbor objects in the measurement field and/or ambient (FLIR T200 user manual (2009). The infrared radiation can be easily reflected from the sample surface into direction of the camera falsifying measurements (Olson and Talghader 2012). The measured temperature may be highly inaccurate when the operator cannot eliminate (or at least minimize) the influence of such external IR radiation sources. The same is related to the proper setting the emissivity *ε* (López *et al*. 2013). It is even more essential when physical modeling of heat and mass transfer within biomaterials is simulated. The availability of experimentally determined *ε* allowed improvement of the FEM models and better representation of the temperature distribution over the building façade as studied within BIO4ever project.

Nevertheless, in several practical applications, such as monitoring of electric connectors/fuses or detecting thermal bridges (moisture spots) in building, the exact value of temperature gradients is not critical. In that case, even tabular values of emissivity may be sufficient for successful qualitative assessments.

CONCLUSIONS

The value of emissivity measured and calculated experimentally for different cladding materials are within the ε range reported in the scientific literature (emissivity of natural wood usually varies from 0.85 to 0.95 according to different authors). Nevertheless, the experimental results revealed noticeable differences in samples of the same wood species but modified with different processes. The emissivity parameters obtained experimentally are essential for precise numerical modelling of the solar radiation and of the moisture content changes in all investigated bio-materials. Consequently, more realistic simulation of the façade appearance and its aesthetical changes become possible (the overall goal of the BIO4ever project).

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Composition of monosaccharides in aqueous extracts from thermally modified wood

Ekaterina Sidorova[1], Olov Karlsson[2] and Dick Sandberg[3]

[1]Department of Wood Science and Engineering, Luleå University of Technology, Forskargatan 1, Skellefteå, Sweden [email: ekaterina.sidorova@ltu.se]
[2]Department of Wood Science and Engineering, Luleå University of Technology, Forskargatan 1, Skellefteå, Sweden [email: olov.karlsson@ltu.se]
[3]Department of Wood Science and Engineering, Luleå University of Technology, Forskargatan 1, Skellefteå, Sweden [email: dick.sandberg@ltu.se]

Keywords: heat treatment of wood, thermal modification, water soluble compounds, aqueous extracts

ABSTRACT

For aesthetic reasons, interest in mould growth on wood for outdoor use in application like claddings has increased during recent years. Products of thermally modified timber are no exception. Thermally modified Scots pine boards have been chemically analysed with regard to their monosaccharide contents. Two industrial thermal modification processes were studied: (1) the ThermoD process in which wood is modified under superheated conditions, and (2) the WTT process in which wood is modified under saturated steam conditions in a closed system. Modified wood samples containing a) only sapwood, b) only heartwood, and c) a mixture of both sapwood and heartwood were chemically analysed with regard to their monosaccharide contents. Different locations (depths) in the cross section of the boards were taken for the analysis. The dried aqueous extract from the modified wood was dissolved in dimethyl sulfoxide, treated with hexamethyldisilazane and trimethylsilyl chloride, and thereafter analysed by gas chromatography (GC-MS). Monosaccharides were identified in the extracts by comparison with the retention times of pure monosaccharides and MS-data. No monosaccharides were found in samples from the ThermoD process, but monosaccharides were present in samples from the WTT process, the monosaccharide content being dependent on by the location of the sample in the cross-section.

INTRODUCTION

According to CEN (2007), thermally modified timber (TMT) is wood in which the composition of the cell wall material and its physical properties have been modified by exposure to a temperature higher than 160 ºC and conditions of low oxygen availability. The wood is altered in such a way that at least some of the wood properties are permanently affected through the cross section of the timber. TMT can be used in a number of outdoor applications such as façades and decking. Outdoor materials are often exposed to high humid conditions and the risk of mould development on their surfaces is therefore higher than under interior conditions. Furthermore, it has been suggested that the colonization of mould on Scots pine boards may be related to the presence of saccharides migrated to the wood surface during the kiln drying of the sapwood (Theander *et al.* 1993).

During thermal modification (TM), wood undergoes changes in its chemical and physical properties involving the partial removal of wood components and the formation of degradation products. Mass losses therefore occur during TM (Hill 2006). Ramiah and Goring (1967) found that pine hemicellulose (glucomannan) starts to degrade at 127 °C, although the degradation temperatures of cellulose and lignin are higher (Fengel and

Wegener 1984). The degradation behaviour of cellulose could be harder to predict than that of hemicelluloses due to its crystalline/amorphous structure; some studies indicate that cellulose components can also start to degrade at lower temperatures than are normally associated with the polymer (Fengel and Wegener 1984). Mitsui *et al.* (2008) suggested that cellulose degrades in the following order: amorphous, semi-crystalline, and crystalline regions. The sugars formed are not stable under TM conditions and may react further into products such as furfural.

The present study has focused on the presence of monosaccharides in sawn timber modified by two different industrial TM processes: ThermoD and WTT. In ThermoD, the timber is treated in air with superheated steam at atmospheric pressure at a maximum temperature of 212 °C. In ThermoD the wood is intended for applications where above ground durability is the key property (International ThermoWood Association 2003). In the WTT process, the timber is treated with saturated steam at a temperature of 170 °C in vacuum under an elevated pressure up to 8 bar (Dagbro *et al.* 2011), and in this process it is possible to achieve modification similar to the ThermoD process, but at a considerably lower temperature (Dagbro *et al.* 2010). Karlsson *et al.* (2012a) have studied extracts of these materials and found that wood from the WTT process had a higher content of saccharides than wood from the ThermoD process. The equilibrium moisture content has been found to be dependent on the position in the thermally modified board, indicating different reactivities across the cross-section (Källander 2016). In the present work, the presence of monosaccharides was studied using GC-MS at different distances from the surface of the TMT.

EXPERIMENTAL

Materials

Wood thermally modified under saturated steam pressure conditions (WTT process)

Scots pine (*Pinus sylvestris* L.) boards containing 80-90% heartwood, with cross-sectional dimensions of 40x150 mm (TxW), were sawn and kiln dried at a sawmill (Stenvalls Trä in Sikfors, Sweden). The sawn timber was thermally modified using the commercial WTT process at 170 °C at Uteträ in Arvidsjaur, Sweden.

Wood thermally modified using superheated steam (ThermoD process)

Scots pine boards containing 80-90% heartwood, with cross-sectional dimensions of 30x125 mm, were sawn and kiln dried at a sawmill (Holmen Timber in Iggesund, Sweden). The timber was thermally modified using the commercial ThermoD process at 212 °C with superheated steam at Heatwood (Hudiksvall, Sweden).

Wood shavings for chemical analysis

Six thermally modified boards were selected for the chemical analyses; three from the WTT process and three from the ThermoD process. Each board was cut to a length of 1 metre and divided into six samples (Figure 1). The samples contained only sapwood (S), only heartwood (H and HM), or a mixture of sapwood and heartwood (SH). The samples were planed on one of their outer-faces (upper faces in Figure 1) with help of a handheld planer to give shavings at depths of:

a) 0.5 mm at S, referred to as SS (sapwood surface);
b) 0.5 mm at SH, referred to as SH (sapwood and heartwood);
c) 0.5 and 1 and 2 and 3 mm at H, referred in to as HS (heartwood surface shaving 0.5 mm) and H1 and H2 and H3 respectively (heartwood shavings at 1, 2 and 3 mm);
d) 0.5 mm at HM, referred to as HM (heartwood middle).

All the shavings were milled into powders.

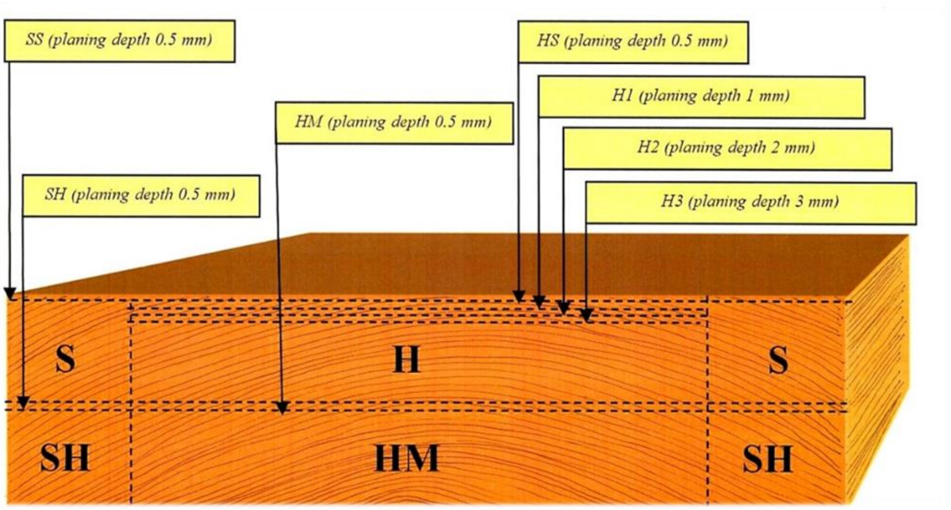

Figure 1: Cross-section view showing how the thermally modified boards were divided into samples for chemical analysis.

Chemical analyses

The wood powder were extracted by soaking in water (200 mg wood powder in 6 mL water) for 2 hours in an ultrasonic bath with no heating and then left in the liquid for 12 hours. The wood powder mixture were then filtered through paper filters into Petri dishes and washed with some water. Thereafter 1 mL of standard methyl β-D-xylopyranoside, 3 mg/ml solution was added to the filtrate in each Petri dish in order to make it possible to calculate the monosaccharide content in the wood samples after GCMS analysis.

The Petri dishes (with the monosaccharide and wood extracts) were left to dry in a hood until all the water evaporated. The dried extracts were each dissolved in 1mL dry dimethyl sulfoxide and transferred to pear flasks. 200 µL hexamethyldisilazane and 100 µL trimethylsilyl chloride were added to each flask, which were shaken with a Vortex mixer. The upper phases of the solutions were analysed with regard to monosaccharide content using gas chromatograph mass spectrometry GCMS-QP5050 (by Shimadzu) using an Agilent VR-23ms column.

Monosaccharides (arabinose, fructose, mannose, galactose, glucose and xylose) were identified in the wood extracts by comparison with the retention times of the pure monosaccharides and MS-data library (NIST107 and NIST21). The contents of the monosaccharides were calculated from the ratio of the monosaccharide peak areas to the standard peak area.

RESULTS AND DISCUSSION

From the GC-MS analyses it was found that the monosaccharides: arabinose, glucose, xylose, mannose and galactose were present in all the extracts from the WTT treated timber. A typical chromatogram is shown in Figure 2. with small amounts of arabinose (retention time (RT) ~ 3 min), glucose (RT ~ 6.8 and 8.5 min) and galactose (RT ~ 6.3 min) but larger amounts of xylose (RT ~ 4 and 4.8 min) and mannose (RT ~ 5.5 min). As other peaks are small, hydrolysis may be the reason for the degradation of polysaccharides (xylans and galactoglucomannans) into the monosaccharides identified in extracts from WTT modified timber. In contrast, monosaccharides were not found in the extracts from ThermoD modified timber, where GCMS chromatogram showed almost only the peak of the added standard compound at RT ~ 3.5 min

(Figure 3). Smaller peaks of oxidised malic (RT ~ 1.7 min), xylonic (RT ~ 3.3 min) and arabinoic (RT ~ 3.4 min) acids were tentatively identified by comparison with mass library data (Figure 3). This could mean that, under the superheated conditions of the ThermoD process, sugars and carbohydrates were partly oxidised by the presence of small amount of oxygen in the process.

Fructose together with glucose and sucrose were found in dried Scots pine wood (Theander *et al.* 1993), but fructose (RT ~ 5.7) was not found in any of the TM samples. Native sugars such as fructose have been reported to be labile during high temperature drying at 110-130 °C (Karlsson *et al.* 2012b).

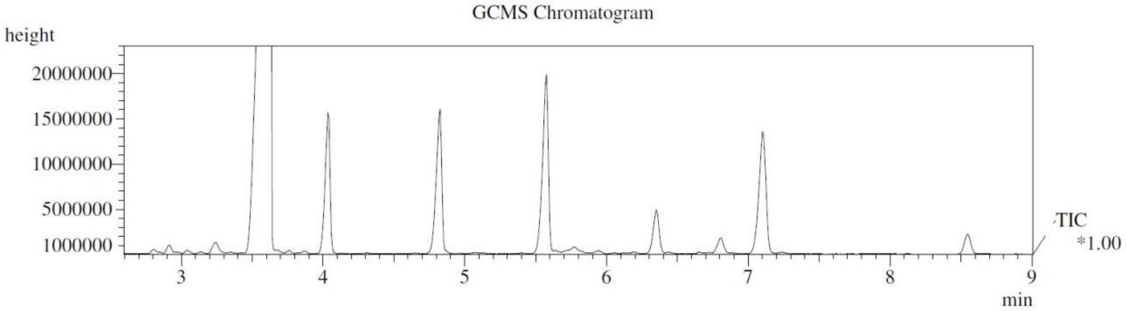

Figure 2: GCMS Chromatogram of WTT-modified timber (heartwood surface samples)

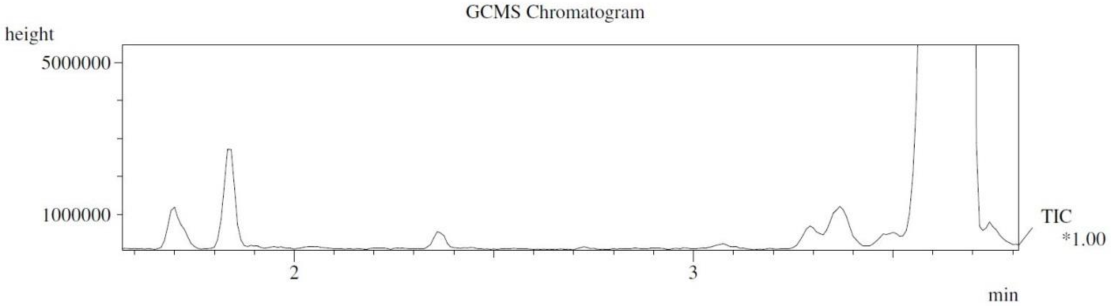

Figure 3: GCMS Chromatogram of ThermoD-modified timber (heartwood surface samples)

Monosaccharides were analysed in samples taken at increasing planing depths from the WTT-modified timber (Table 1, Figure 4). A higher content of xylose was found at the surface than deeper into the sawn timber. The mannose content was higher at the surfaces of heartwood (sample HS) than further from the surface in heartwood (sample H3 and HM). The differences between arabinose and glucose contents were not significant. Comparing the total amounts of monosaccharides (arabinose, glucose, xylose, mannose and galactose) in different parts of the timber, it was found that the total average monosaccharide content was higher in the samples containing a mixture of heartwood and sapwood (samples SH) than in the other samples. The mannose content varied greatly in the SH samples so it is difficult to conclude that SH samples had the highest monosaccharide content compared with the other samples. There was a tendency for the monosaccharide content to be higher at the surfaces of both heartwood and sapwood.

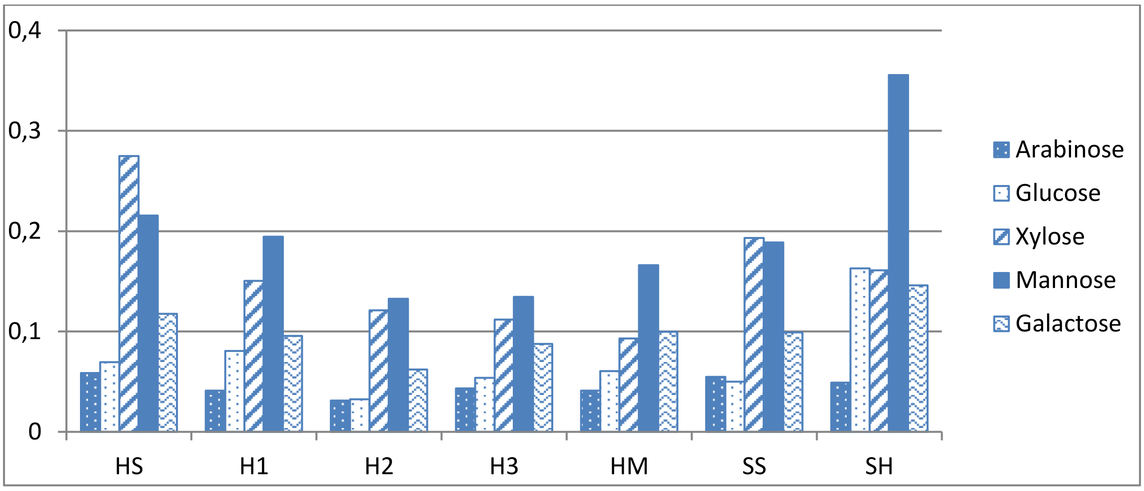

Figure 4: Water-soluble monosaccharides in WTT-modified timber: dependence on sample location in the cross section (in mg per 100 g of dry wood)

Table 1: Monosaccharide content in WTT-modified timber

Mono-saccharides	HS[a]	H1[a]	H2[a]	H3[a]	HM[a]	SS[a]	SH[a]
Arabinose	0.059 (0.03)[b]	0.041 (0.02)	0.031 (0.03)	0.043 (0.02)	0.055 (003)	0.055 (0.05)	0.049 (0.02)
Glucose	0.069 (0.02)	0.081 (0.1)	0.033 (0.03)	0.054 (0.06)	0.061 (0.02)	0.050 (0.03)	0.163 (0.1)
Xylose	0.275 (0.14)	0.151 (0.09)	0.121 (0.09)	0.112 (0.06)	0.093 (0.04)	0.193 (0.14)	0.161 (0.04)
Mannose	0.216 (0.03)	0.195 (0.17)	0.133 (0.13)	0.134 (0.12)	0.166 (0.05)	0.189 (0.13)	0.356 (0.15)
Galactose	0.118 (0.04)	0.096 (0.08)	0.062 (0.06)	0.088 (0.03)	0.100 (0.03)	0.099 (0.07)	0.146 (0.06)
Total sum	0.736	0.563	0.380	0.431	0.475	0.586	0.874

[a]*Average values in mg per 100 g of dry wood;* [b]*standard deviations in parentheses.*

CONCLUSIONS

No water-soluble monosaccharides were found in ThermoD modified timber, whereas arabinose, glucose, xylose, mannose and galactose were found in WTT-modified timber. There is a tendency for the monosaccharide content to be higher at the surfaces of the WTT-modified timber than in the inner sections.

ACKNOWLEDGEMENTS

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Insights into stability of glued joints between thermally modified timber: adaptation of an artificial weathering test

Morwenna Spear[1], Raisa Teciu[1] and Graham Ormondroyd[1]

[1]The BioComposites Centre, Bangor University, Deiniol Road, Bangor, LL57 2UW, U.K.
[email m.j.spear@bangor.ac.uk]

Keywords: adhesion performance, dimensional stability, thermal modification, weathering

ABSTRACT

Thermal modification leads to enhanced dimensional stability among other property changes. There is interest in using mild thermal modifications to add value to joinery products. A mild-modification system for Welsh timber has been developed to improve dimensional stability and working properties of fast grown softwoods such as larch (*Larix kaempferi*) and Western hemlock (*Tsuga heterophylla*). There is potential to combine this with lamination to achieve large section pieces suitable for joinery applications. This paper reports a set of tests developed to investigate the strain within glued joints in modified wood under combined wetting, UV and humidity cycling regimes.

The developed method was based on EN 927-6, which is a QUV artificial weathering test typically used to evaluate the performance of coatings on wood. By omitting a mask, and allowing UV exposure over the total surface, the glued joints within the samples were exposed to rapid drying during the UV phases of the cycle and wetting during spray cycles. This places significant strain on any paint films or glue joints, providing a challenging test method, enabling comparison of film performance and bonding. After six days cycling between spray and UV the samples were removed and placed above a water bath to provide elevated humidity on the underside (uncoated face). This had the effect of permitting asymmetric swelling through the thickness of the sample. Samples were removed from the QUV chamber between each one week cycle, to gather data relating to moisture content, degree of splitting, checking or delamination.

The samples were prepared from modified Japanese larch. Pieces were planed and laminated with four lamellae using a polyurethane adhesive. In the final piece the lamellae were aligned radially, tangentially or half-radially or half-tangentially, laid up to minimise and to maximise strain at the glue-line by deliberately favouring matching (e.g. radial to radial) or poor (e.g. tangential to radial) combinations. In addition, combinations of mild and moderate thermal modification were placed in adjacent glue-lines. Samples were tested uncoated, or with clear varnish coating on only the upper face.

Swelling in tangential dimensions of the segments was greater than in the radial dimensions, resulting in visible difference of thickness where radial-tangential bonds had been created. However bonding remained good through the 12 week period. The performance of a high gloss varnish was also monitored, and only minor defects observed in the majority of segments. The observed dimensional changes, moisture uptake and development of splits and checks within the wood will be discussed to illustrate stress development within the laminated samples. The results clearly highlight the potential of this test method as a severe combination of cyclic conditions, with potential for evaluating adhesive performance under asymmetric conditions.

INTRODUCTION

Thermal modification is a well-established form of wood modification, leading to enhanced dimensional stability among other property changes. It may be used to add value to readily available timbers, not only due to greater suitability for joinery products resulting from reduced moisture movement but also aesthetic benefits. Development of a mild-modification system for Welsh timber was motivated by a desire to improve dimensional stability and working properties of fast grown softwoods such as larch (*Larix kaempferi*) and Western hemlock (*Tsuga heterophylla*) (Spear *et al.* 2016). Lamination of these thermally modified timbers was proposed as a method to achieve large section pieces suitable for joinery applications such as window components. As a result a set of tests was developed to investigate the strain within glued joints in modified wood under combined wetting, UV and humidity cycling.

A test method was developed and trialled, based on EN 927-6, which is a QUV artificial weathering test typically used to evaluate the performance of coatings on wood. By omitting a mask, and allowing UV exposure over the total surface, the glued joints within the samples were exposed to rapid drying during the UV phases of the cycle (90 mins), and wetting during spray cycles (30 mins). This places significant strain on the glue joints, and any paint films or covering. The aim was to find a challenging test method for rapid evaluation and comparison of glueline and film performance. After the six days UV and water spray cycle, the samples were moved and placed above a water bath to provide elevated humidity on the underside (uncoated, or unexposed face) for one day. This had the effect of permitting asymmetric swelling through the thickness of the sample. Samples were observed between each one week cycle, to gather data relating to moisture content, degree of splitting, checking or delamination.

EXPERIMENTAL

Sample material and preparation

Samples of modified Japanese larch were generated by a mild and a moderate treatment intensity thermal modification process as described in Spear et al. (2015). Pieces were planed and laminated into workpieces with four lamellae using a polyurethane adhesive. Once cured the work pieces were rip sawn perpendicular to the glued joint to provide samples containing 4 segments and three glued joints (Figure 1a,b). The samples were then re-planed to give a smooth finish prior to varnish coating. The dimensions of the samples for the weathering test were 150x74x18 mm

The samples were prepared with the lamellae aligned radially, tangentially or half-radially or half-tangentially, so that the growth rings within segments were aligned parallel, perpendicular or at an intermediate angle to the plane of the test sample. The lamination of the pieces was designed to minimise and to maximise strain at the glue-line by deliberately favouring matching (*e.g.* radial to radial) or poor (e.g. tangential to radial) combinations of growth ring alignment. In addition, combinations of mild and moderate thermal modification were placed in adjacent glue-lines (Figure 1b).

Figure 1a: Laminated samples after cutting and planing to the required thickness. Small matching samples for moisture uptake study were cut from the ends of the longer weathering samples. 1b: End grain of a selection of moisture content samples, showing matched and non-matched grain orientation within the laminate

Much is known about the ideal lay-up for laminating wood for joinery applications, for example selecting the location of the pith within adjacent pieces, and orientation of growth rings; however within a high throughput environment this process may be time consuming, or not possible for long lengths of timber. The test deliberately generated poorly matched samples to maximise likelihood of defects.

Moisture content

From each laminate two matched moisture samples were cut. These were conditioned at 20°C and 65% r.h. for one week until stable. Pieces were matched, allowing maximum moisture uptake to be observed on soaking without oven drying (leaching would alter an oven drying value after soaking), and determination of an oven dry value for never soaked material. Weight and dimensions in the conditioned state was recorded for all samples.

To determine the maximum moisture content, one set of the conditioned samples were placed in a beaker under ballast and a vacuum applied (20 min.), then soaked, by introducing deionised water while the samples were still on the vacuum. The weight and dimensions were recorded when fully soaked.

The other set of moisture content samples were oven dried, and weight and dimensions recorded. The determined value for conditioned moisture content was used in calculating estimated oven dry weights for the matching sample material.

Weathering test to observe laminate performance

Weathering exposure samples were tested either uncoated or coated. The coating was a transparent marine varnish (International Paints), applied as two coats on only one face. The coated face was the face exposed to the UV and the simulated rainfall. The weathering test was based on EN 927-6, but omitted a mask, allowing UV light to access the entire upper face of the sample. Samples were removed, measured and observed at each one week cycle to determine dimensional change and development of any defects. Three cycles were performed and evaluated here.

RESULTS AND DISCUSSION

Moisture content test observations

The moisture soaking test revealed the maximum dimensional change likely within the samples (Figure 2). Distortion resulted from differences in swelling between laminae, and diamonding of laminae where grain orientation favoured this, e.g. in the ½ radial or ½ tangential or intermediate (45°) pieces.

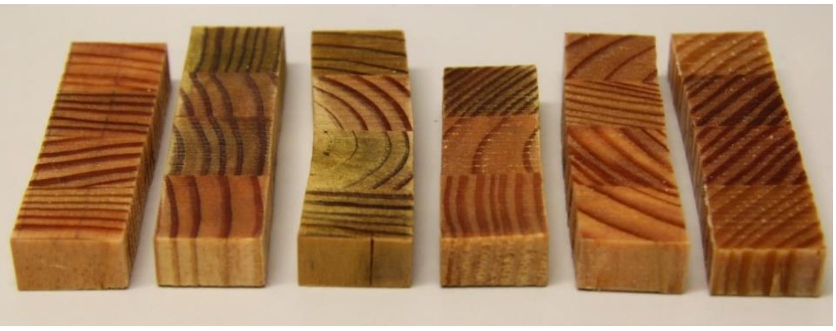

Figure 2: Moisture content samples reveal maximum deformation of the sample due to dimensional change

Table 1: Moisture content test

Sample	Weight after soaking	Estimated weight in dry state	Total weight uptake	% moisture content	Conditioned weight	Conditioned moisture content
A1b	14.36	7.80	6.56	84.10	8.62	10.51
B1b	15.41	8.31	7.10	85.44	8.96	7.82
C1b	14.87	6.93	7.94	117.98	7.44	7.36
D1b	12.19	6.36	5.83	91.67	6.85	7.70
E1b	15.27	7.39	7.88	106.63	8.11	9.74
F1b	17.32	8.19	9.13	111.48	8.94	9.16

Table 2: Dimensional change (%) on complete wetting

Sample	Average segment 1	Average segment 2	Average segment 3	Average segment 4	Largest difference	Measurement pair and notes	
A1b	8.34 T	7.59 T	7.74 ½T	7.57 T	0.71	9-10	1/2Tan to Tan
B1b	3.80 R	3.78 R	3.54 ½R	8.15 R	4.39	9-10	Moderate to Mild
C1b	6.38 T	2.71 1/2R	3.95 ½R	5.50 ½T	2.16	3-4	1/2Tan to 1/2Rad
D1b	5.12 R	2.16 R	4.92 ½R		2.46	3-4	Mature to Juvenile
E1b	4.35 int	8.22 ½R	6.67 int	6.43 int	2.75	3-4	Juvenile to mature
F1b	7.49 int	3.39 int	3.74 int	6.98 int	2.25	9-10	Mature to juvenile

Note: T = tangential, R = radial, ½T = half tangential, ½R = half radial, int = intermediate or 45° growth ring alignment. These are recorded for the measurement direction, i.e. the thickness of the laminate.

The moisture content of the pieces was relatively consistent on conditioning (7.3 to 10.5%, Table 1), with the variability likely reflecting differences in numbers of mild and moderate treated pieces within the laminated sample, and their density (*e.g.* relating to juvenile wood).

The change in thickness was measured at twelve locations on each sample, i.e. three locations per strip within the laminate – at the edge middle and edge. Average percent change in thickness within a single strip is presented in Table 2, and reveals a larger change for samples in the tangential than the radial orientation, as expected. It is this difference which was harnessed in the weathering test, to induce stress in the glued joints. The greatest difference between pairs of measurements at a joint were also noted in Table 2. Examination of the soaked samples revealed that large differences in the observed swelling related to combinations of grain angle, combinations of the mild and moderate treatment intensity, and combinations of juvenile wood with more mature wood.

Weathering test to observe laminate performance

In the weathering test, the growth ring orientation, intensity of treatment and presence of juvenile wood again influenced the swelling seen between strips with in the laminates. However bonding remained good through the full test period (Figure 3).

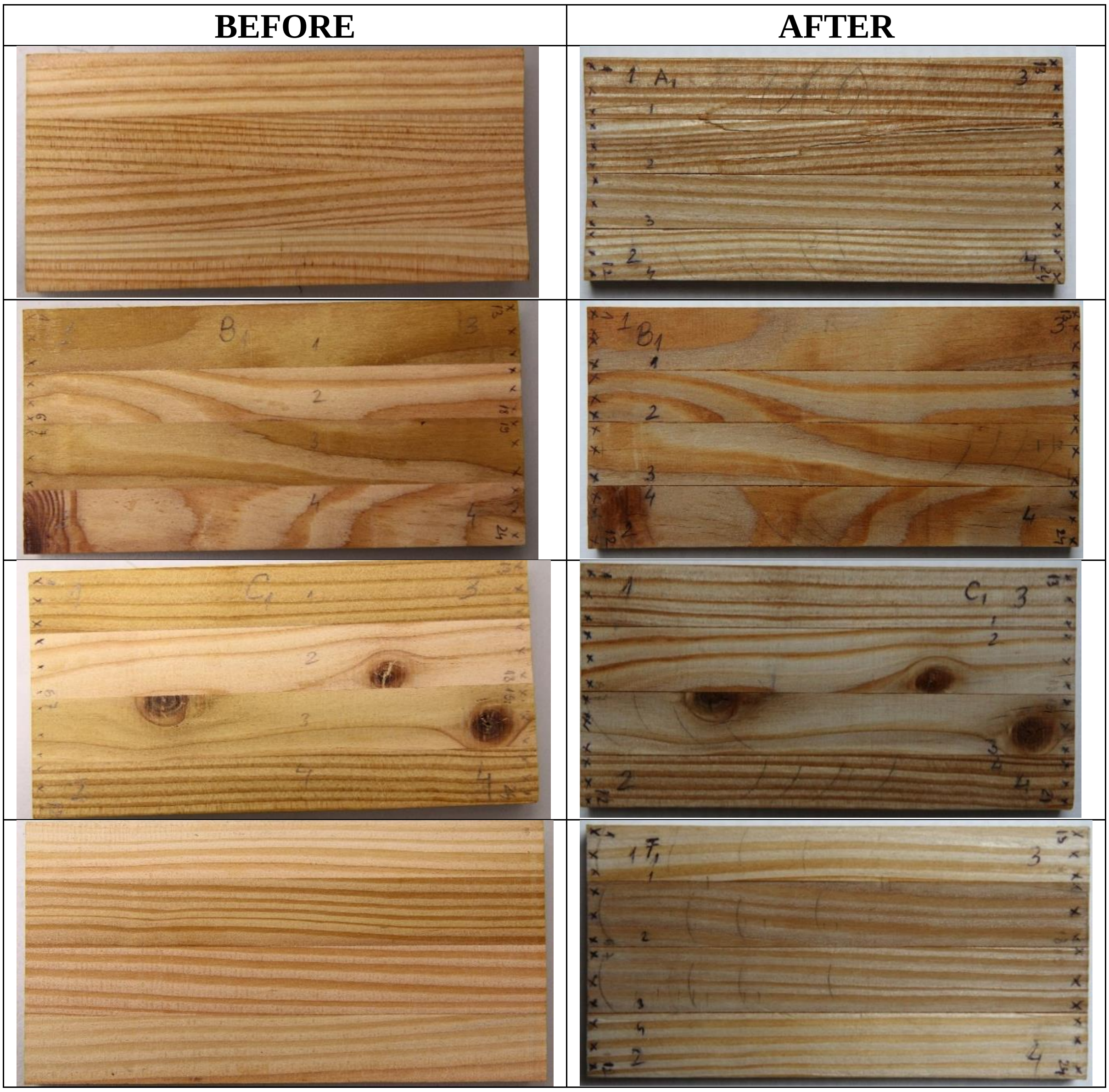

Figure 3: Photographs of samples A1b, B1b, C1b and F1b before and after QUV weathering exposure

Samples were examined after each week long conditioning cycle, and any splits, checks or delaminations were marked. Development of splits relating to knots was the most common fault. Checking in the end grain was observed in many pieces, but was minor, as would be seen in exposed end grain of joinery. One sample developed a radial split which led to a defect within the weathered face. After the second cycle, no new faults were seen on the third cycle.

The performance of a high gloss varnish was also monitored in a separate set of samples (not shown), and only minor defects in the varnish coating were observed in the majority of segments.

CONCLUSIONS

The presented results demonstrate that the mild and moderate thermal treatment in larch was successful in lamination trials. The differential swelling and shrinkage at glue joints did not lead to failures during the test period. The test deliberately generated poorly matched laminae within the samples to maximise likelihood of defects occurring during the test. Therefore the low incidence of defect formation despite high differences in swelling (up to 4.39%) between adjacent laminae was satisfactory, indicating the suitability of mild thermally modified larch for further development.

The results also clearly highlight the potential of this test method to provide a severe combination of cyclic conditions, with potential for evaluating adhesive performance under asymmetric conditions. The humidity differential generated by the conditioning stage of the cycle led to cupping in all samples at the end of the week, demonstrating the moisture gradient across the samples.

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Water resistant tannin polymers

Gianluca Tondi[1] and Lukas Sommerauer[2]

[1]Salzburg University of Applied Sciences, Forest product technology & Timber constructions dept., Marktstr. 136a, A-5431, Kuchl [email: gianluca.tondi@fh-salzburg.ac.at)]
[2]Salzburg University of Applied Sciences, Forest product technology & Timber constructions dept., Marktstr. 136a, A-5431, Kuchl [email: lsommerauer.htw-m2017@fh-salzburg.ac.at)]

Keywords: Bio-based copolymers, Bioresources, Crosslinking, Networking, Polyflavonoid.

ABSTRACT

One of the major drawbacks for the use of industrial tannin extracts for wood preservation purposes is their leachability. In the past years the idea of fixing tannin in wood by *in-situ* polymerization was deeply investigated and the principal results that were obtained can be summarized with plenty of positive findings: increased mechanical properties, enhanced fire resistance, good penetrability and interesting biological resistances. Modified formulations containing small amount of boron or copper showed also good resistances against fungi, insects and even termites. In these formulations, the tannin polymers showed interesting capacity of limiting the leaching of biocide, warranting an extended preservation activity. However, it was also observed that a certain leaching of the tannin polymers occurs regularly, especially in the first exposure to water when the unreacted molecules were quickly solubilized. In order to find a more performing tannin-based formulation for wood protection, a systematic study was conducted analysing the water resistances of different copolymerization partners of tannin at various temperatures. Hexamine and formaldehyde were used as reference hardeners, while glyoxal, maleic anhydride, furfural and furfuryl alcohol were considered as potential alternatives. Study of pH and relative amount have allowed to identify several interesting tannin-based copolymers for replacing the tannin-hexamine of the previous investigations. It was observed that furfural and glyoxal are able to crosslink the tannins at every of the investigated pHs, while furfuryl alcohol and maleic anhydride are effective only in acid environment. All of these formulations require high hardening temperature but they produce bioplastic with more than 60% of water resistance. These formulations have been tested also in wood applying higher hardening temperature (140 °C) and they have shown superior water resistance properties with less than 20% material loss.

INTRODUCTION

After lignin, the tannins are the more abundant aromatic substance on our planet (Arbenz & Averous, 2015; Missio *et al.* 2017). These polyphenols are produced by superior plants for protecting their vegetal tissues from biologic agents and free radicals (Hagerman et al. 1998). For this reason, tannins are mostly concentrated in the areas where the plants are more vulnerable and namely: bark, core, leaf and seeds. According to different wood species the amount of tannins varies from traces until 20-30% (Kryn, 1954) and it has been proven that the wood species containing higher amount of these molecules are more durable (Scalbert 1992; Taylor *et al.* 2002; Kirker *et al.* 2013). Unfortunately, the most common European timbers for construction (e.g. spruce, pine, beech) are relatively poor in tannins and they present also limited durability (Durability class 4 or 5) (EN350-2, 1994).

Due to their intrinsic biologic role, these extracts have been extensively studied as wood preservatives (Tascioglu *et al.* 2013) and in every study involving leaching significant mass loss was registered due to their water solubility (Sen *et al.* 2009; Thévenon *et al.* 2010). Also when the tannins were fixed with hexamine, a certain initial loss could not be completely avoided because the conditions applied did not allow to completely crosslink all the components (Tondi *et al.* 2012). The smaller fractions and the non-phenolic components of the extract were considered as an unavoidable lost.

In this contribution we present a systematic polymerization study of alternative tannin-based copolymers hardened at different temperature and pH. Formaldehyde, hexamine, glyoxal, maleic anhydride, furfural and furfuryl alcohol were tested as co-monomers to produce stable polymers with tannins and then polymerized in wood. The resistance against leaching of the polymers and of the treated wood in function of the hardening parameters is shown.

EXPERIMENTAL

Different tannin formulations were synthesized in sealed test-tube by adding hardeners to a 20 g tannin solution (33,3%) in water at specific pH level (2, 4.5, 7 and 9). The polymerization tests are summarized in Table 1.

Table 1: Tannin copolymers preparation

Hardener	**Amount [%s./s.tannin]**	**pH**	**Min. Hardening temperature [°C]**
Formaldehyde	4,6,8,25	2,4.5,7,9	20
Hexamine	4,6,8,25	2,4.5,7,9	50
Glyoxal	4,6,8,25	2,4.5,7,9	90
Maleic anhydride	6,12.5,25,50	2,4.5	103
Furfural	6,12.5,25,50	2,4.5,7,9	50
Furfuryl alcohol	6,12.5,25,50	2,4.5,7,9	90

The all the experiments were successively at kept for 24 h at the temperature of 20,50, 70, 90 and 103 °C and at then removed from the tube, grinded, further dried at 60 °C and then finally milled to fine granulometry (<300 µm). 1g of these powders were then leached in 100 ml deionized water under magnetic stirring or one hour. The suspensions were then filtered and dried so that the amount of insoluble was quantified for each tannin copolymer (Tondi, 2017).

The more promising copolymers were then used for impregnating beech samples using a 10% tannin solution infiltrated through a vacuum process with cycles of 30 min vacuum and 24 hours impregnation. The samples were then dried at 140 °C for different time (2,6, 16 and 40 hours) and their leaching resistances were quantified by washing with 10 times v./v. water through cycles of 1, 2, 4, 8 and 16 h under moderate mechanical shaking. The samples were then dried at 103 °C until constant weight to evaluate the amount of polymer remained (Sommerauer *et al.* 2018).

RESULTS AND DISCUSSION

The powders of the tannin copolymers dried at 103°C and grinded presented interesting leaching resistances which are summarized in Figure 1.

It can be observed that all the formulations tested presented more than 60% leaching resistance, and only the polymers of maleic anhydride at strongly acid pH did not reach 70%. In particular, it was observed that the polymers of furfural and furfuryl alcohol, respectively in alkaline and acid environment, reached leaching resistances higher than 80% and comparable with the well-known tannin-formaldehyde and tannin-hexamine formulations.

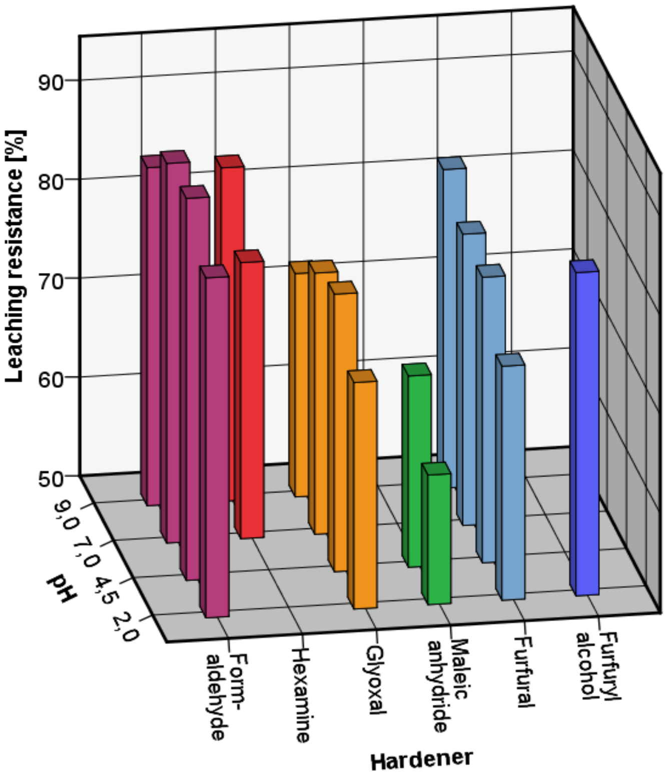

Figure 1: Leaching resistance of different tannin copolymers

These results confirmed that the products obtained after these processes are co-polymers. The leached part was attributed to the fact that the original industrial tannin extract is constituted by a 20-30% of non-tannins. These materials are carbohydrates and in particular the most of them are hydrocolloids. We believe that the leached material is constituted by fractions of unreacted phenolics combined with part of these hydrocolloids.

These formulations were then tested as wood preservatives by applying an enhanced polymerization temperature of 140 °C and different hardening time. The results of the leaching are reported in figure 2. General increase in the fixing was observed by increasing the hardening time. For formaldehyde, hexamine and furfural the trend was almost linear with similar slopes. This suggests similar cross-linking kinetic patterns which confirms the polymer properties observed also during the leaching of the copolymers. Instead, the copolymers with furfuryl alcohol, glyoxal and maleic anhydride show a steeper slope suggesting a higher dependence to heat. For the polymers of glyoxal and maleic anhydride we observe that even if they were the less water-resistant at 103 °C, they became the more leaching resistant when polymerized at 140 °C in wood. Further, they are the only reaching more than 90% resistance after 40 hours. This phenomenon could be interpreted in two ways: i) a more extensive/effective polymerization, which involves also the non-tannin part and ii) a possible grafting of these polymers in wood.

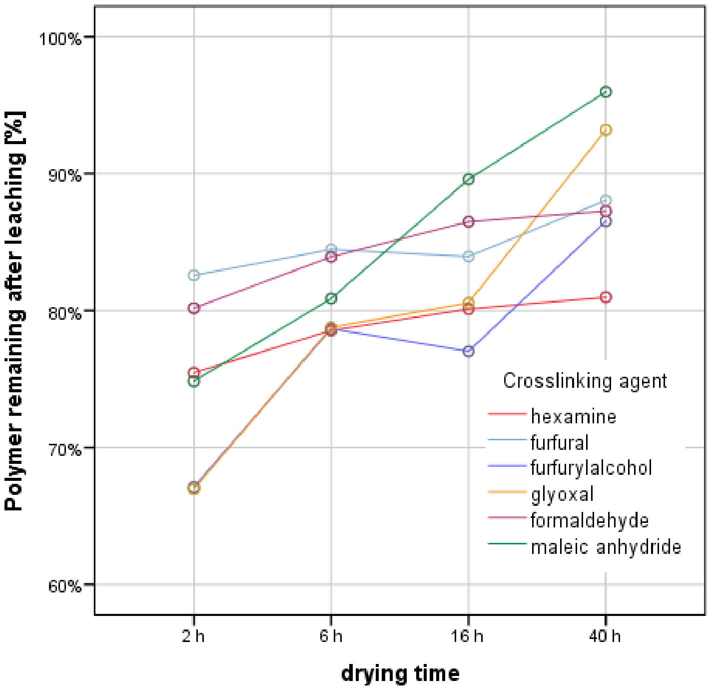

Figure 2: Leaching resistance of the tannin-based formulation at 140°C

This trend suggests that the tannin-based copolymers with milder hardening time have more chances to crosslink in a way that result more water-resistant during the operative time.

CONCLUSIONS

Tannin copolymers are a broader family of compounds: Not only formaldehyde and hexamine can be used for producing stable macromolecules. Furfural, for instance, showed similar polymerization patterns to the classical hardeners; furfuryl alcohol very high resistance in acid environment; while glyoxal and maleic anhydride have shown the need for longer heating session in order to produce more water resistant polymers.

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Dynamic and static mechanical properties of *Eucalyptus nitens* thermally modified in an open and closed reactor system

Maximilian Wentzel[1], Christian Brischke[1], Holger Militz[1]

University of Goettingen, Wood Biology and Wood Products, Buesgenweg 4, 37077 Goettingen, Germany
[email: mwentze@gwdg.de]

Keywords: *Eucalyptus nitens*, High-Energy Multiple Impact (HEMI) test, modulus of elasticity (MOE), modulus of rupture (MOR), thermal modification

ABSTRACT

Eucalyptus nitens is a fast growing plantation species that has a good acclimation in Chile. There is a growing market for solid wood products made from this species and an interest on producing high quality material out of it. Thermal modifications offer a good alternative to do this. In this study we modified *E. nitens* and evaluated its mechanical properties to check if it complies with the necessary standards to be a competitive product. The material was modified in a closed system under elevated pressure and controlled relative humidity (30 and 100% RH) at temperatures between 150 and 170°C, and in an open system with a standard thermal modification procedure between 160 and 230°C. Modulus of elasticity (MOE), modulus of rupture (MOR), deflection and work in bending (in elastic and inelastic proportions) and the resistance to impact milling (RIM) in High-Energy Multiple Impact (HEMI) tests were determined. Mass loss after each modification was also measured and correlated with the mechanical properties.

INTRODUCTION

Currently, *E. nitens* plantation wood is mostly used for pulp and paper or biofuels, but there is an interest to widen the use of this fast growing tree species in Chile. Thermal modification offers an alternative to produce high quality material and opens potential markets for the use of this species. These processes use treatment temperatures between 150°C and 240°C and different operating conditions, either steam, vacuum, nitrogen or other elements that limit the presence of oxygen in the process (Hill, 2006, Militz and Altgen, 2014). They can be separated in open systems, in which the modification happens at atmospheric pressure (ThermoWood (Mayes and Oksanen, 2002)), and closed systems, where the processes work under steam pressure (FirmoLin (Willems, 2009)) or under vacuum. The wood composition changes when it is exposed to high temperatures, modifying its dimensional stability and its mechanical properties (Esteves and Pereira, 2009). These variations are also closely related to the species and the process conditions. The static modulus of rupture (MOR) and the modulus of elasticity (MOE) are affected differently, as the MOR tends to reduce more than the MOE, as shown for thermal modification of birch (Poncsák *et al.*, 2006) and beech (Tjeerdsma *et al.*, 1998). In both species, MOE and MOR reduced with rising modification temperature. In contrast, it was shown that the MOE of *Eucalyptus globulus* (Santos, 2000) and *Betula papyrifera* (Canadian white birch) (Lekounougou *et al.*, 2011) increased in certain thermal modifications. Other mechanical properties, such as the structural integrity of wood, are also affected by the thermal modification. A test was developed to determine the structural integrity of wood in relation to its resistance to impact milling (RIM). This is determined in High-Energy Multiple Impact

(HEMI) tests, which had been designed using steel balls of different size in a heavy vibratory mill for crushing wood samples. The process was developed to overcome the drawbacks of standard dynamic strength tests. Instead of using a high number of replicate wood specimens, the number of events that affect directly the wood were multiplied (Brischke *et al.*, 2006, Brischke, 2017). It is measured by the RIM, which varies between 0 and 100%, indicating the structural integrity of the wood.

The objective of this study was to examine the static (MOE and MOR) and the dynamic mechanical behavior (HEMI test) of eucalypt wood after treatments in both open and closed reactor systems to analyze the influence of the process conditions.

EXPERIMENTAL

Material

E. nitens wood that derived from 19 year old plantations of the Región del Bío-Bío in Chile was used. Wood specimens with dimensions of 20 × 50 × 650 mm^3 (radial x tangential x longitudinal) were prepared from kiln-dried wood that had an average moisture content (MC) of 12% avoiding large knots and other visible flaws. For each modification process ten specimens were used.

Thermal modification processes

Thermal modifications in open and closed system were performed. The open system was a process similar to the Thermowood procedure (Mayes and Oksanen, 2002), in which the process has a pre-drying step that starts at 100°C up to 130°C at a heating rate of 2°C per hour. Afterwards the temperature ramps up at 12°C per hour to the peak temperature, where it is hold up for 3 hours. Finally, the temperature decreased at a rate of 20°C per hour to 65°C. In the case of the closed system modification, the WTT process (Willems, 2009) was used. It had four steps: a 50 min holding step at pre-vacuum at <14 kPa, temperature increase in a rate of 12°C per hour until modification temperature, a holding step at the peak temperature for 3 hours and a temperature decrease in a rate of 20°C per hour up to 65°C. The total duration of the process was shorter in the closed system than in the open system. The list of modifications is presented in Table 1. Both processes were performed at a laboratory scale reactor in a stainless steel vessel that was connected to an external water reservoir and a gas washer with steerable valves (Willems, 2009).

The final wood MC was measured after each modification by difference of dry weight using small pieces collected from each specimen, so that this value could be extracted from the dry weight of each specimen. The degradation products of the cell wall carbohydrates accumulate in the wood during modifications at high temperatures (Altgen *et al.*, 2016). Hence, for a correct measurement of mass loss, the extractive content was measured as described by the Solvent Extractives of Wood and Pulp Test Method T 204 cm-07 (TAPPI, 1997) using a Soxhlet apparatus. The corrected mass loss (CML) was calculated based on the dry and extractive-free weight of the wood before (unmodified) and after each process. It should be noted that the wood specimens were neither dried nor extracted prior to each modification process.

Table 1: Peak temperature, maximum pressure, extractive content, corrected mass loss (CML), moisture content (MC) and total process duration (TPD) of both modifications (open and closed) and the relative humidity (RH) applied in the thermal modifications in the closed systems. Duration of the modification at peak temperature was 3 hours for all processes.

Open System

Peak temperature (°C)	Max pressure (mPa)	RH (%)	Extractives (%)	CML (%)	Final MC (%)	TPD (h)
160	atmospheric	-	6.76	5.37	3.34	30
180	atmospheric	-	9.04	7.89	2.04	33
200	atmospheric	-	12.29	14.61	2.04	35.5
210	atmospheric	-	12.70	18.68	2.18	37
220	atmospheric	-	9.12	16.78	2.25	38
230	atmospheric	-	7.44	19.29	2.44	39.5

Closed System

Peak temperature (°C)	Max pressure (mPa)	RH (%)	Extractives (%)	CML (%)	Final MC (%)	TPD (h)
150	0.14	30	5.96	2.55	4.50	16.5
160	0.18	30	7.64	4.99	3.85	18
170	0.23	30	8.41	6.29	3.20	19
150	0.47	100	12.72	11.36	5.27	16.5
160	0.61	100	13.16	18.57	4.94	18
170	0.77	100	10.05	20.51	4.62	19

Mechanical properties

A three-point bending test according to DIN 52186 (1978) was conducted using a universal testing machine (Zwick Roell Z010, Zwick, Ulm, Germany) to measure the modulus of elasticity (MOE) and the modulus of rupture (MOR) (both in Nmm^{-2}) of wood specimens of 10 × 10 × 180 mm^3 (radial × tangential × longitudinal) that were conditioned at 20°C/65% RH before the test. At least 15 replicates per modification were tested. The span length of the specimens was 150 mm and the load was applied in the transversal direction with the testing speed adjusted individually for each modification to allow failure of the samples within 90±30 s. A load decrease of 10% or more of the maximum load was defined as failure. The elastic deflection (δ_e) (mm), inelastic deflection (δ_i) (mm) and work in bending (W_{max}) (N mm), which was separated into inelastic and elastic proportions (W_e (N mm) and W_i (N mm) respectively) were measured using the formulas described by Altgen and Militz (2016).

The development of the HEMI test had been described by Rapp *et al.* (2006). In the present study, the process was adapted from the procedure presented by Brischke (2017): 20 oven dry specimens of 10 x 10 x 10 mm were placed into a bowl of 140 mm inner diameter of a heavy impact ball mill (Herzog HSM 100, Osnabrück, Germany), together with one steel ball of 35 mm diameter, three steel balls of 12 mm diameter, and three steel balls of 6 mm diameter. The bowl was shaken for 60 s with a rotary frequency of 23.3 s^{-1} and a stroke of 12 mm. The fragments of the 20 specimens were fractionated on a slit sieve with a slit width of 1 mm using an orbital shaker at an amplitude of 25 mm and a rotary frequency of 350 min^{-1} for 2 min. The following values were calculated using Eqn. 1, Eqn. 2 and Eqn. 3:

$$I = {}^{m_{20}}/_{m_{all}} * 100\ (\%) \qquad (1)$$

Where the degree of integrity (I) is the ratio of the mass of the 20 biggest fragments (m_{20}) to the mass of all fractions (m_{all}) after the crushing process.

$$F = {}^{m_{<1mm}}\!/_{m_{all}} \tag{2}$$

Where the fine fraction (F) is the ratio of the mass that is sieved and has a diameter of less than 1 mm ($m_{<1mm}$), to the mass of all fractions (m_{all}) multiplied by 100.

$$RIM = {}^{(I - 3 * F) + 300}\!/_{400}\ (\%) \tag{3}$$

Where RIM is the resistance to impact milling and represents the value of the measure for the structural integrity of the material. All results for the static and dynamic mechanical properties are presented as a ratio with the average value of the reference set to 1, which means that any value above 1 was better than the reference and any value below 1 means a decrease of the property.

RESULTS AND DISCUSSION

The static and dynamic mechanical properties of the modified *E. nitens* wood samples were analyzed as a function of the CML (Figure 1).

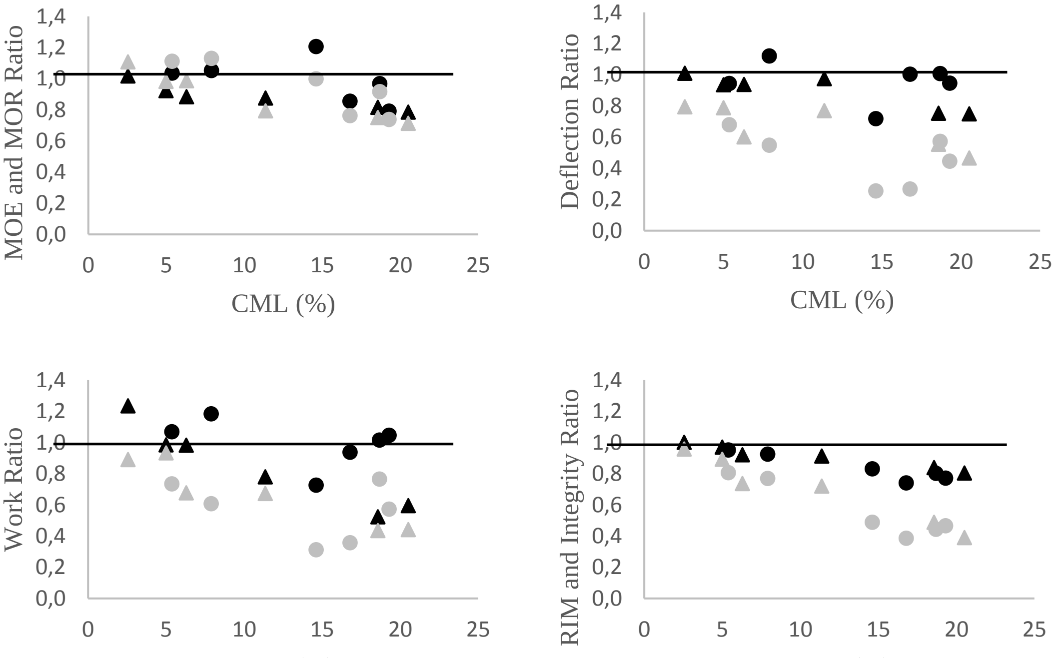

Figure 1: ***Ratio of MOE, MOR, inelastic and elastic deflection and work, RIM and integrity as a function of CML. Circles represent open system modifications, triangles represent closed system modifications. Black represents MOE, elastic deflection, elastic work and RIM; grey represents MOR, inelastic deflection, inelastic work and degree of integrity. The line shows the unmodified reference value.***

The MOR ratio did not decrease at CML below 10% (Figure 1). At CML above 10% the MOR ratio decreased up to 0.71 at 170°C and 100% RH, while at 230°C in the open system modification showed the highest decrease in the ratio (0.74). In the case of the MOE ratio, it slowly decreased when the CML was above 10%, but it was less than the MOR ratio. In the open system modification there was an increase of the MOE ratio until 200°C, after that point it started to decrease but without showing a direct relation between the CML and the MOE. The variation of MOR ratio may be related to the hemicelluloses, as they tend to degrade at higher modification temperatures and play an important role in the strength of wood (Esteves and Pereira, 2009) and to a decrease in the equilibrium moisture content (Borrega and Kärenlampi, 2008). As for the MOE there was a constant decrease of its ratio in the closed system, whereas there was a peak at 200°C, similar to what was reported by Santos (2000) in a thermal modification of *E. globulus*, although no type of treatment was mentioned.

The elastic deflection decreased with increasing CML in all the closed system modifications, while in the open system modification it was at its lowest at 200°C (0.72) and showed almost no variation in all other temperatures. On the other hand, the inelastic deflection was more sensitive to the thermal modification as it decreased further than the elastic deflection as the temperature rose on all the closed system modifications. The open system modifications showed a lower inelastic deflection ratio than in the closed system (Figure 1), with its lowest peak being at 200°C (0.25). The results were similar to what was obtained in European beech (Altgen and Militz, 2016) and Norway spruce (Borrega and Kärenlampi, 2008). In the case of the open system, it only had one specific modification (at 200°C) that presented a low inelastic deflection ratio. This could be an influence of the material properties in that particular modification, such as microscopic defects or density.

Elastic work ratio was higher at the lowest CML and then it decreased as the temperature rose in the closed system modifications at 30% and 100% RH. At the open system it slightly increased at the lowest CML, reaching its lowest point at 200°C (0.73). At higher CML the elastic work showed no variation in relation to the reference sample. The inelastic work had a similar tendency as the elastic work in all the closed system modifications, meanwhile the closed system had its lowest ratio at 200°C (0.31) (Figure 1). The changes could be associated to the inelastic deflection, as it influences the plastic flow, thus influencing negatively the work in bending. As for the closed system, it showed similar tendencies as the deflection, but with slightly higher ratios.

The RIM as well as the degree of integrity decreased as the temperature increased for both open and closed system modifications. The slight differences between the modifications could be related to changes at cell wall level, as the RIM is directly correlated with the decrease in microstructural integrity caused by heat-induced modification of the cell walls (Welzbacher *et al.*, 2011).

When directly comparing two processes with similar CML from the open and closed system, the process at 160°C and 100% RH and the process at 210°C had similar values (18.57% and 18.68% respectively), there were some differences in all the ratios of their respective static mechanical properties but similar values in the dynamic mechanical properties. The differences were more noticeable when comparing the chemical changes, as described by Wentzel *et al.* (2018).

CONCLUSIONS

In general, there was not a huge difference between open and closed system modifications in the variation of mechanical properties in relation to their CML. Closed system modification had slightly lower vales than open system modifications in the static mechanical properties, but no difference in the dynamic mechanical properties. Only mechanical properties are not enough to show differences between open and closed modification systems. Further investigations on the anatomical and chemical changes would give additional explanation on the differences between both systems.

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SESSION EIGHT

Performance

Enhancing the material properties of wood through furfurylation

Wanju Li[1,2,3], Changhua Fang[1,2], Hankun Wang[1,2], Xuexia Zhang[1,2] , Dan Ren[1,2]
and Yan Yu[1,2] *

[1] Department of Biomaterials, International Center for Bamboo and Rattan, Beijing, China [email: cfang cfang@icbr.ac.cn; yuyan9812@icbr.ac.cn]
2 SFA and Beijing Co-built Key Lab for Bamboo and Rattan Science & Technology
[3] Guangdong Provincial Key Laboratory of Silviculture, Protection and Utilization, Guangdong Academy of Forestry, Guangzhou, China

Keywords: Furfurylation, wood, durability resistance to mould, decay fungi, termite

ABSTRACT

Due to its potential for commercial applications, wood modification with furfuryl alcohol (FA) is now attracting enhanced attentions from researchers and industry. In this study, Chinese Fir (*Cunninghamia lanceolata*) and poplar (*Populus tomentosa*) were modified with furfuryl alcohol which is catalysed by a new composite acidic catalyst through a common vacuum and pressure process. The orthogonal experiments with three factors (FA concentration, curing temperature and time) and four levels were designed to obtain the optimized furfurylation process for the two tree species. The weight percent gain (WPG), equilibrium moisture content at 23℃ and 65% relative humidity (EMC), anti-swelling efficiency (ASE) and the resistance to mould, decay fungi and termites were evaluated. The results showed that nearly all the properties were improved to some different extent by FA treatments. The EMC of furfurylated Chinese fir and poplar decreased to 8% and 6%, respectively. The maximum ASE of furfurylated poplar wood could reach as high as 90% in volume, while for Chinese fir, the maximum ASE was 75%. The furfurylated modification endowed Chinese fir and poplar wood excellent properties of anti-mould, decay fungi and termite resistance. No visible growth of mould was found on treated specimens. The treated specimens were all in durability class “I” (very durable) regarding to decay fungi resistance with weight loss ratios (WLR) less than 6%. After termite tests, the WLRs of treated specimens were all less than 1%, which were significantly less than those of untreated ones.

INTRODUCTION

Both Chinese fir and poplar are the most important fast grown plantation wood species in China. Fast-growing wood species have the advantage of short-rotation, but their performance defects are also very obvious, including dimensional changes in response to altering atmospheric humidity, susceptibility to biological attack and changes in appearance when exposed to outdoor conditions (Hill 2007). They have lower natural durability resisting mould, fungi and termite, which limits their application, leading to much shorter service life and lower commercial value. Wood preservation is one of the most effective methods to prevent damage caused by biological attack, using some toxic preservative. However, due to environmental concerns toxic preservative as PCP-Na and CCA have been limited or banned (Cristensen *et al.* 2005; Nguyen *et al.* 2012). Alternative methods to protect wood from biological attack is to modify the surface and internal structure of wood, such as heat treatment, acetylation and furfurylation. Wood furfurylation has been recognized as an efficient strategy for improving resistance against moulds and fungal decay during the service period (Lande *et al.* 2004a; Hadi *et al.* 2005; Pan *et al.*, 2015). The modification method has been described to tack place through different reactions (Lande *et al.* 2008; Sejati *et al.* 2016): (1) homo-polymerization of furfuryl alcohol (FA), (2) co-polymerization and reaction with cell wall components, and (3) grafting of FA to wood cell wall polymers. The possible mechanism could be the reduction of void volume through bulking or change of the chemical nature of the cell wall via possible cross-linkage between FA and wood cell wall (Venås 2008; Pilgård and Alfredsen 2009; Lande *et al.* 2004b). During furfurylation process catalysts play a very important role. They should give the FA formulation long pot life, as well as ensure rapid polymerization when heated. Furthermore, the catalyst should have a small molecular weight, as well as similar affinity for wood substances and FA, as this ensures deep penetration into wood cell wall without separation from FA. The catalysts used mostly were maleic anhydride or citric acid. We have proposed a new composite acidic catalyst for wood furfurylation in previous study, which showed that the physical mechanics of the furfurylated wood catalyzed by the new composite acidic catalyst produced comparable results to maleic anhydride with much less FA required (Li *et al.* 2015).

The objective of this study was to evaluate the durability, as well as hygroscopicity and dimensional stability, of furfurylated Chinese fir (*Cunninghamia Lanceolata*) and poplar (*Populus tomentosa*) wood catalysed by a new composite acidic.

MATERIAL AND METHODS

Wood materials preparation

Chinese fir (*Cunninghamia Lanceolata*) and poplar (*Populus tomentosa*) were used in this study. Specimens, 10 mm×20 mm×50 mm,10 mm×20 mm×20 mm and 20 mm×20 mm×50 mm (radial × tangential×longitudinal) were used for mould, decay and termite tests, respectively, and 20 mm×20 mm×20 mm (radial × tangential×longitudinal) for moisture content and dimension stability tests.

Table 1. Orthogonal experimental design for different test groups and the corresponding WPGs.

Group	FA Concentration (%)	Curing Temperature [℃]	Curing time [h]	WPG [%] Chinese Fir	WPG [%] poplar
1	15	95	1.5	25±4.2	18±1.2
2	15	105	3	34±3.2	21±2.5
3	15	115	5	54±13.5	30±4.1
4	15	125	8	60±15.7	30±2.4
5	30	95	3	50±16.8	34±3.6
6	30	105	1.5	27±4.9	20±2.6
7	30	115	8	70±11.6	54±4.7
8	30	125	5	56±8.6	49±3.2
9	50	95	5	52±9.5	50±6.4
10	50	105	8	86±12.7	66±4.8
11	50	115	1.5	44±9.9	38±4.6
12	50	125	3	62±16.1	39±5.7
13	70	95	8	63±12.9	31±7.0
14	70	105	5	49±9.1	37±2.5
15	70	115	3	78±16.1	40±13.3
16	70	125	1.5	39±9.5	24±3.9

Furfuryl alcohol treatments

Furfuryl alcohol solutions were prepared at room temperature containing FA, water, buffering agent and catalyst. The catalyst used was a compound organic acid composed of oxalic acid and citric acid. The buffering agent was used to adjust the pH of solutions within the range of 3 to 4. A custom-built reactor (PF-2) was applied to impregnate FA into wood specimens using vacuum-pressure process. This process consisted of a period of treatment in vacuum for 30 min followed by 0.5 MPa of pressure for 3 h, then immersion in FA solutions for 36 h at normal pressure. The wood specimens impregnated were then wrapped in aluminum foil to avoid the evaporation of solution during the curing stage. After polymerization, the treated samples were gradually dried at 60℃ and 80℃for 2 hours, respectively, and then oven-dried. Different FA concentrations, curing temperatures and curing durations were used and the orthogonal experiments were designed as shown in Table 1.

The weight percent gain (WPG) was calculated according to equation (1):

$$WPG = ((M_1 - M_0)/M_0) \times 100\% \qquad (1)$$

where M_1 and M_0 were the oven-dry weight of the specimens after and before FA treatments, respectively.

Hygroscopicity and dimensional stability measurements

Equilibrium moisture content (EMC) at 20°C and 60% relative humidity (RH) was measured to determine the effect of FA treatments on wood hygroscopicity. Measurements were performed on both treated and untreated specimens.

The most frequently used term for quantifying dimensional stability is anti-swelling efficiency (ASE), defined as follows:

$$ASE = ((S_0 - S_1)/S_1) \times 100\% \qquad (2)$$

where S_0 was the swelling of untreated specimens and S_1 was the swelling of treated specimens. Swelling (S) is calculated as:

$$S = ((V_w - V_o)/V_o) \times 100\% \qquad (3)$$

where V_o was the volume at oven-dry condition and V_w was the volume at 25°C and 96% RH.

Mould resistance tests

Mould resistance tests were conducted according to Chinese National Standard GB/T 18261-2000. In brief, *Aspergillus niger* V.Tiegh, *Penicillam citrinum* Thom, *Trichoderma viride* Pers.ex Fr and *Botryodiplodia theobromae* Pat were incubated on potato agar culture medium in Petri dishes and cultivated in an incubator at 22-25 ℃and 85% RH for 7 days. After mycelium permeated the culture dish, they were then placed in the incubator for another 4 weeks. During this period, the extent of mould attack (surface area percentage) was recorded. Mould growth on wood specimens was rated according to Chinese National Standard GB/T 18261-2000 as shown in table 2.

Table 2. Standard method for rating of the mould infection according to GB/T 18261-2000

Rating	Description
0	No visible growth
1	Mould covering up to 10% of the surface
2	Mould covering between 10% and 30% of the surfaces
3	Mould covering between 30% and 70% of the surfaces
4	Mould on greater than 70% of the surfaces
5	Mould on 100% of the surfaces

Decay fungi resistance tests

Fungal decay resistance was evaluated according to Chinese National Standard GB/T 13942.1-2009. White rot fungi *Coriolus versicolor* (CV) and brown rot *Gloeophyllum trabeum* (GT) were used for tests. Dry weights of furfurylated and untreated wood samples were measured before they were exposed in flasks, where the decay fungi had been inoculated. The flasks were then placed at conditions of 25 ± 2℃ and 85 ± 5% RH for 8 weeks. The decay resistance was evaluated by the weight loss ratio (WLR_f) according to equation (4) and evaluated the classes of wood durability to decay fungi according to table 3:

$$WLR_f = ((M_2-M_3)/M_2) \times 100\% \qquad (4)$$

where M_2 and M_3 were the weight of the specimens before and after infection of decay fungi, respectively.

Table 3. Classes of wood durability to decay fungi according to GB/T 13942.1-2009

Durability class	**Description**	**Weight loss ratio**
I	very durable	0~10%
II	Durable	11%~24%
III	Slightly durable	25%~44%
IV	Not durable	＞45%

Termite resistance tests

The tests on the resistance of samples against Formosan subterranean termites (*Coptotermes formosanus* Shiraki) were evaluated according to Chinese National Standard GB/T 18260-2015. The efficacy of the treatment was evaluated based on the weight loss ratio of the materials due to termite attack. Five test blocks for treatment group were randomly selected and conditioned at 23℃ and 65% relative humidity for days until they reached a constant weight. Then the blocks were measured before they were placed in sterilized test bottles filled with sand. The bottles were then sterilized at 138℃ and 0.25 MPa for 2 h. About 500 termites comprising 10% soldiers and 90% workers were introduced in each of the test bottles. They were conditioned in a conditioning room maintained at 28 ±2 ℃ and 80±5% relative humidity overnight. The bottles were then covered with black papers and kept at room temperature (25-27℃) for a period of 4 weeks. At the end of the test period, the blocks were removed and cleaned. They were again left in 23℃ and 65% relative humidity for days until their weights were constant. The weight loss ratio (WLR_t) was calculated according to equation (5):

$$WLR_t = ((M_4-M_5)/M_4) \times 100\% \qquad (5)$$

where M_4 and M_5 is the oven-dry weight of the samples before and after infection of termites, respectively.

At the end of the first and fourth weeks, the containers were examined and the presence of tunnelling, termite mortality, and position of the termites in the container were observed.

RESULTS AND DISCUSSION

WPG, EMC and ASE

Table 1 shows the results of WPGs. The higher FA concentration, higher curing temperature and longer curing time treatment could have positive effect on WPG to a certain degree. WPG of treated Chinese fir wood increased from 42% to 61% and that of treated poplar wood increased from 24% to 48% with rising FA concentration from 15% to 50%. Esteves *et al.* (2011) treated Pinus pinaster with 70% FA mixture and got only an average WPG of 38%. The results of this study indicate that Chinese fir and poplar wood have good capability to accommodate FA. It is worth noting that WPG decreased obviously with FA concentration rising to 70%. This result can be explained by the fact that FA could not polymerize well and volatilize with low curing temperature and short curing time.

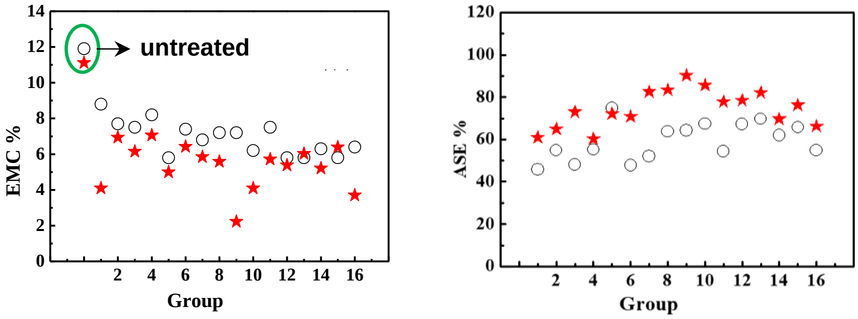


Figure 1. The EMC and ASE of Chinese fir (circle) and poplar (star) in different treated groups.

The EMCs of all furfurylated wood samples remarkably decreased (Figure 1). The EMC of untreated Chinese fir and poplar wood were 11.9% and 11.1%, respectively, while that of furfurylated Chinese fir and poplar wood samples reduced to 8% and 6%, respectively. Analogous results were reported by Epmeier *et al.* (2007), who also observed an obviously decreased of EMC for furfuylated Pinus. The blocking effect of FA resin inside the wood cavity and even the cross-linkage with the wood cell wall component, which definitely decreases the absorption of water molecules in wood, is likely the main cause for this significant reduction in EMC. The reduction in moisture uptake might contribute to inhibiting fungi growth in furfurylated wood (Ringman *et al.* 2014).

The dimensional stability was improved significantly for both Chinese fir and poplar. The average ASE of furfurylated Chinese fir and poplar wood can reach as high as 75% and 90%, respectively, in volume (Figure 1). The high ASE might be caused by the decrease of moisture absorption and the restriction effect of impregnated FA.

Mould resistance

The untreated Chinese fir wood and poplar showed little resistance to Aspergillus niger V. Tiegh and Botryodiplodia theobromae Pat mould and became rapidly covered with mould mycelium. The infection process of P. citrinum and T. viride was slower, there is less mycelium appeared on the surface of Chinese fir wood than on the surface of poplar wood. After one month of testing, the mould resistance rating against Aspergillus niger, Botryodiplodia theobromae, P. citrinum and T. viride reached 3, 2, 2 and 4, respectively, for untreated Chinese fir and 4, 3, 3 and 4, respectively, for untreated poplar. In contrast, furfurylated Chinese fir and poplar wood showed excellent anti-mould properties. The ratings against the four kinds of mould were all “0”, even the WPG of furfurylated wood was only 15%. The significant improvement of anti-mould might be attributable to the blockage of the entering channels of mould by FA. Additionally, another possible reason was that the moisture content of furfurylated bamboo decreased significantly and the pH value changed.

Decay fungi resistance

The untreated Chinese fir wood show a noticeable mass loss caused by CV and GT with an average WLR_f of 45.13% and 45.82%, respectively. While specimens of furfurylated Chinese fir and poplar woods showed no apparent decay, and the WLR_f was all less than 6%. According to table 3, furfurlated Chinese fir and poplar wood tested were classified very durable, while the untreated Chinese fir and poplar wood tested were classified not durable and little durable, respectively. Figure 2 shows the relationship between the WPG of furfurylated wood and WLR_f of furfurylated wood infected by decay fungi. The high WPG could have positive effect on the durability of furfurylated wood. The WLR_f of furfurylated Chinese fir and poplar wood decreased with increased WPG.

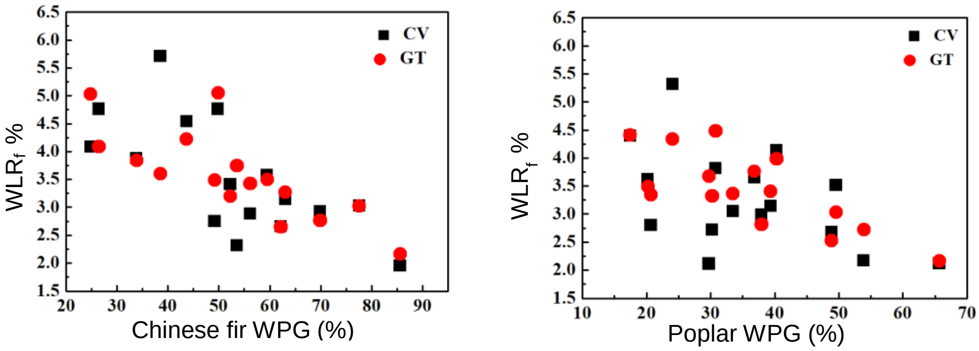


Figure 2. Relationship between the WPG of furfurylated wood and WLR_f of furfurylated wood infected by decay fungi

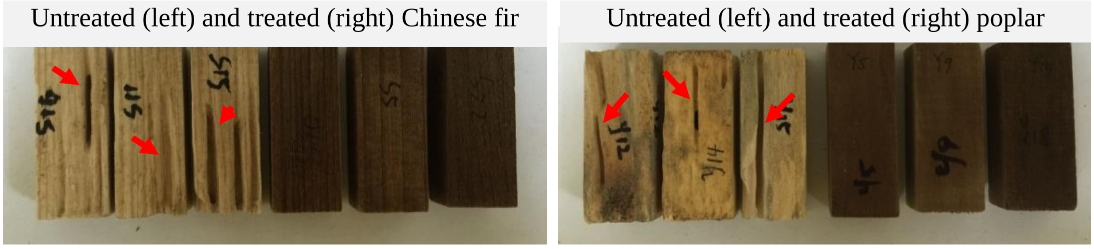
Compare to similar studies on the durability of furfurylation of wood catalyzed by maleic anhydride or citric acid, durability of furfurlated wood catalyzed by compound organic acid composed of oxalic acid and citric acid was better. The possible reason is the function of oxalic acid which has certain bactericidal properties, except that furfuryl-based resins block the access way of decay fungi into wood and the chemical change of cell wall by possible cross-linkage between FA and wood cell wall components (Pilgård and Alfredsen 2009; Lande *et al.* 2004b).

Termite resistance

Termites can cause serious damage to wooden structures (Pan *et al.* 2015). In this study, the WLR_t of furfurylated specimens of was was significantly less than untreated ones for both Chinese fir and poplar (Table 4). Mass losses of untreated Chinese fir and poplar were 8.54% and15.51%, respectively, while mass losses were between 0.66% and 1% for furfurylated Chinese fir and poplar. There was no visible nibble trace on the surface of furfurylated apecimens attacked by termites (Figure 3). But the untreated Chinese fir and poplar wood were eaten by termites along their full length (Figure 3). On the fifth day of the test, lots of termites were found on the surface of untreated wood blocks, but few on the surface of the furfurylated wood (Figure 4). After tests, termite's survival rate were 46.2% and 48.2% on untreated Chinese fir and poplar, respectively. In comparison, there was about 30% termites was survival in the test of low- and high- furfurylated Chinese fir wood, whereas no survival termite in furfurylated poplar specimens (Table 4).The results indicated that termites didn't like FA, and the FA might act as a poison to termites.

Table 4. The results of termite resistance tests

Species	Treatment	WPG [%]	WLR$_t$ [%]	Survival rate [%]
Chinese fir	untreated	0	8.54	46.2
	treated	20~30	0.69	34.2
		90~110	1	30.5
poplar	untreated	0	15.51	48.2
	treated	15~25	0.66	0
		60~90	0.81	0


Untreated (left) and treated (right) Chinese fir

Untreated (left) and treated (right) poplar

Figure 3. Pictures of treated and untreated Chinese fir and poplar after termite attack test. Arrowheads show the termite attack traces.


Untreated (left) and treated (right) poplar

Figure 4. Pictures of treated and untreated poplar after 5-day termite test.

CONCLUSIONS

In this study, Chinese Fir (*Cunninghamia Lanceolata*) and Poplar (*Populus tomentosa*) were modified with furfuryl alcohol catalysed by a new composite acidic catalyst through a common vacuum and pressure process. The treatments significantly decreased moisture absorption with low EMC and increased dimensional stability with high ASE. The furfurylation endowed Chinese fir and poplar wood excellent properties of anti-mould, decay fungi and termite resistance. No visible growth of mould was found on treated specimens. The treated specimens were all in durability class “I” (very durable) regarding to decay fungi resistance with weight loss ratios (WLR) less than 6%. After termite tests, the WLRs of treated specimens were all less than 1%, which were significantly less than those of untreated ones.

ACKNOWLEDGEMENTS

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Comparative studies on the biological durability of identical thermally modified wood from field and laboratory tests

Sven Hertrich[1], Lothar Clauder[1], Silke Lautner[1], Alexander Pfriem[1]

[1]Faculty of Wood Engineering, Eberswalde University for Sustainable Development, Alfred-Möller-Strasse 1,
16225 Eberswalde, Germany [email corresponding author: sven.hertrich@posteo.de)]

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ABSTRACT

Thermal modification changes wood's chemical composition and enhances its biological durability and dimensional stability. The aim of this study was to validate findings from laboratory studies following EN 113 (1996) with field tests according to EN 252 (1990, 2015) after five years of exposure. Thermally modified European beech and Norway spruce with various treatment intensities were used. The decay rates, degradation velocities, and the durability factors were determined to classify the durability (DC) inspired by EN 350 (2016).The modified beech wood treated at 220 °C reached classification DC 2 (durable). Modified spruce achieved DC 4 (slightly durable) at most. For the durability classification of the beech samples from the soil contact test, a possible relationship was found to the laboratory test with *Trametes versicolor*. For the modified spruce samples, remarkable differences were found between both durability tests referring to *Trametes versicolor*. A slight agreement with *Gloeophyllum trabeum* was detected. The DC classes of the test specimens from the soil contact tests were lower in both wood species.

INTRODUCTION

To determine the biological durability of wood and wood products, various field and laboratory test methods are used. In Europe, biological durability is determined by field tests using EN 252 (2015), laboratory testing against basidiomycetes using EN 113 (1996), or the soft rot test using CEN/TS 15083-2 (2005). Wood in the field trial, installed in the ground, is subject to the greatest load. Usually, the test situations of EN 252 (2015) were used. These tests represent installation situations of use class 4 (UC 4) and are time-intensive (Augusta 2007; Alfredsen and Westin 2009). The classification is typically done in accordance with EN 350 (2016), in a five-level system from durability class 1 (DC 1, very durable) to durability class 5 (DC 5, not durable). To achieve comparable results in a short period of time, investigations are conducted with a combination of laboratory and outdoor tests, so called "semi-field tests" (Brischke *et al.* 2014). The anatomical structure and chemical composition determine the biological durability of wood. The accessory ingredients (e.g. carbohydrates, waxes, lipids and terpenoid compounds) that serve as a natural protective mechanism because of their biocidal compositions are of great importance, as they notably affect the resistance to wood-destroying organisms. The concentration and variety of accessory compounds of wood-preserving substances are particularly high in tropical woods. Thus, these woods have very good resistance against wood-destroying organisms and uses for outdoor applications (*e.g.*, terrace structures). Over the last two decades, enhanced efforts have been undertaken to develop alternative and environmentally friendly wood protection methods. Thermal modification of wood could establish itself as a progressive method. Various processes for the thermal modification of wood are marketable (*e.g.* the PLATO method or the Thermowood process). With these processes thermal wood modification was able to be established as an advanced method. By modifying the cell wall components, properties of the wood substance can be improved. Increasing biological resistance to wood-destroying organisms is considered the most notable positive effect of thermal modification. Depending on the type of wood and the process used, increased durability is temperature- and time-dependent (Hill 2006). In general, the various treatment processes increase the biological resistance against wood-destroying organisms, making wood more versatile in outdoor applications. The following factors regarding the increased biological durability of thermally treated wood have been described by several authors: increased wood hydrophobicity and limited sorption of water, yielding unfavourable conditions for the development of wood-destroying microorganisms; fungicidal extracts produced by the modification process; modification of wood polymers such that the enzymes responsible for wood degradation do not regard the resulting fungicidal extractives as nutrients; and significant decomposition of hemicelluloses, which serve as a major nutrient source for wood-destroying microorganisms (Welzbacher *et al.* 2008; Metsä-Kortelainen and Viitanen 2009).

This study reports the comparative investigations of the biological durability of identical specimens from individual in-ground field tests and laboratory tests. The investigation consisted of the evaluation of the field trials with soil contact. The biological durability in soil contact and the degradation behaviour of the specimens were taken into account. In the comparative study, the data obtained from the laboratory were compared with the results of the field trial. The main focus was the durability classification.

EXPERIMENTAL

Wood material and thermal modification

Wood of European beech (*Fagus sylvatica* L.), Norway spruce (*Picea abies* (L.) H. Karst.), and Scots pine sapwood (*Pinus sylvestris* L.) were used for this study. To prepare the modification process, the wood was sawn into pieces of 70 mm × 35 mm × 1500 mm (tangential × radial × longitudinal) and dried to wood moisture of approximately 12%. The raw pieces of beech and spruce woods were used for thermal modification. Native Scots pine and batches of untreated beech and spruce woods served as controls. From then on, the controls were described according to EN 13566 (2003) with the trading names FASY, PCAB, and PNSY. The thermal modification process was conducted in a pilot system and comprised a non-pressurised three-stage heating method in nitrogen atmosphere to avoid oxidation during the treatment. With different treatment intensities ranging from 180 °C for 2 h to 220 °C for 10 h, the raw pieces were thermally modified. After conditioning, the wood material was sawn for the particular test methods. For EN 252 (1990), the dimensions were 25 mm × 50 mm × 500 mm; for EN 113 (1996), 6 mm × 20 mm × 20 mm. Table 1 presents the specimens for both situations.

Table 1: Test specimens to determine the biological durability in ground contact (EN 252 1990) and in laboratory tests (EN 113 1996)

Type of Wood – Treatment Intensity		**Number of Test Specimens for Laboratory Test (EN 113 1996)**			**Number of Test Specimens for Field Test (EN 252 1990)**
		Trametes versicolor	***Oligoporus placenta***	***Gloeophyllum trabeum***	
European beech (*Fagus sylvatica* L.)	FASY	40	40	40	20
	180 °C 2 h	12	12	12	12
	180 °C 6 h	12	12	12	12
	180 °C 10 h	12	12	12	12
	200 °C 2 h	12	12	12	12
	200°C 6 h	12	12	12	12
	200 °C 10 h	12	12	12	12
	220 °C 2 h	12	12	12	12

Type of Wood – Treatment Intensity		**Number of Test Specimens for Laboratory Test (EN 113 1996)**			**Number of Test Specimens for Field Test (EN 252 1990)**
		Trametes versicolor	***Oligoporus placenta***	***Gloeophyllum trabeum***	
	220 °C 6 h	12	12	12	12
	220 °C 10 h	12	12	12	12
Norway spruce (*Picea abies* (L.) H. Karst.)	PCAB	-	-	-	20
	180 °C 2 h	10	10	10	10
	180 °C 6 h	10	10	10	10
	180 °C 10 h	10	10	10	10
	200 °C 2 h	10	10	10	10
	200°C 6 h	10	10	10	10
	200 °C 10 h	10	10	10	10
	220 °C 2 h	10	10	10	10
	220 °C 6 h	10	10	10	10
	220 °C 10 h	10	10	10	10
	PNSY	-	-	-	20

In-ground test in accordance with EN 252

In accordance with EN 252 (1990, 2015), the test series was launched in spring 2011 and completed in autumn 2016. The dimensions of the test field with field soil were 14 m × 4 m. To evaluate the biological durability for wood in ground contact, the specimens were buried according to EN 252 (1990). The degradation ranking of each test specimen was determined with a visual inspection and a pick test twice per year. For the visual test, the test specimens were inspected for the presence of decay and described by the assessment criteria in the first table of EN 252 (1990, 2015). The so-called “pick test” was realized with a cutter knife. To evaluate the effects of microbial activity of the soil substrate and to investigate the durability factor (Eqn. 3), the degradation velocities (Eqn. 1) regarding to the exposure time were determined,

$$v_{Dgr} = AB / t_P \qquad (1)$$

where v_{Dgr} is the degradation velocity (degradation stage / year), AB is the degradation rating after past exposure period (degradation stage 0 to 4), and t_P is the past exposure period (year).

The durability values x (Eqn. 2) were determined according to EN 350 (2016). The durability value expresses the average service life of the test specimens towards the most durable batch in relation to that of the controls,

$$x = LT_P / LT_R \qquad (2)$$

Because not all test specimens failed during the exposure time, the durability classification according to the degradation rankings was established with the durability factor f as a provisional assessment (Eqn. 3). The durability factor was calculated as the quotient of the degradation velocity of the controls and the degradation velocity of the tested specimens. With Eqn. 3, the durability classes DC 1 (very durable) to DC 5 (not durable) were determined,

$$f = v_R / v_S \qquad (3)$$

where f is the durability factor, v_R is the average degradation velocity of the controls (degradation rate / year), and v_S is the average degradation velocity of the test specimens (degradation rate / year).

Resistance test against basidiomycetes in accordance with EN 113

The resistances of thermally modified beech (*Fagus sylvatica* L.) and spruce (*Picea abies*) against basidiomycetes were tested by Richter (2011) in accordance with EN 113 (1996) and have been realised with beginning the in-ground field test in 2011. For each treatment intensity and test fungus, 12 beech and 10 spruce samples were investigated (Table 1). The incubation time of three monoculture test fungi (*Trametes versicolor*, *Oligoporus placenta*, and *Gloeophyllum trabeum*) was 16 weeks. With the determined percentage mass loss (ML), the durability classification towards basidiomycetes (DC 1 to DC 5) was established according to Table D.1 in CEN/TS 15083-1 (2005). Because the current EN 350 (2016) covers the distribution of test results, for this study, the determined data for thermally modified beech and spruce wood were prepared, analysed, and evaluated according to this standard.

RESULTS AND DISCUSSION

Durability classification

Decay rates

The controls of beech wood completely failed before the end of the exposure time. Rapid and intensive degradation of untreated beech wood in soil contact has already been shown in many studies (Brischke *et al.* 2014; Stirling *et al.* 2016). Scots pine was the most resistant of the controls. From the treatment intensity 200 °C for 6 h, the positive effect of the thermal treatment was detected from the declining degradation rates. Furthermore, a delayed onset of wood degradation was achieved in succession of increasing treatment intensities during the biannual evaluations. Intense microbial activity was indicated by a quick progression of high decay rates, especially regarding to the controls of beech wood. This indicated that beech wood was more susceptible to white and soft rot than conifers. Due to the anatomical structure of hardwood lignin (GS-lignin), a greater susceptibility of beech wood to white and soft rot than conifers could be assumed (Schmidt 2006; Alfredsen and Westin 2009). Through lower degradation rates and the longer service life of the control conifers, the infestation by white rot or soft rot is strengthened in this study. Regarding modified spruce wood, the degradation activities until the treatment intensity of 200 °C for 6 h were similar during the second, third, and fourth years. The initialization of the degradation was delayed with increasing treatment intensity. Similar observations were made for modified beech wood for specimens treated at 220 °C for at least 6 h. From this and from the aforementioned lower degradation ratings of the control conifers it results that predominantly white rot or soft rot prevail and therefore a delayed degradation of modified spruce occurs.

Degradation velocity

With increasing treatment intensity, a decreasing progression of the degradation velocity was determined. This indicates an increase in biological durability and a longer service life for intensely treated beech wood test specimens. Modified spruce exhibited a slight degradation velocity with increasing treatment intensity. On the whole, this process was slower in contrast with the modified beech specimens. No batch of any treatment intensity failed before the end of the exposure time, showing slow degradation of these modified test specimens. These results correlated with a study by Brischke *et al.* (2014), which reported that microbial wood degradation is retarded by a sandy soil substrate

Durability factor

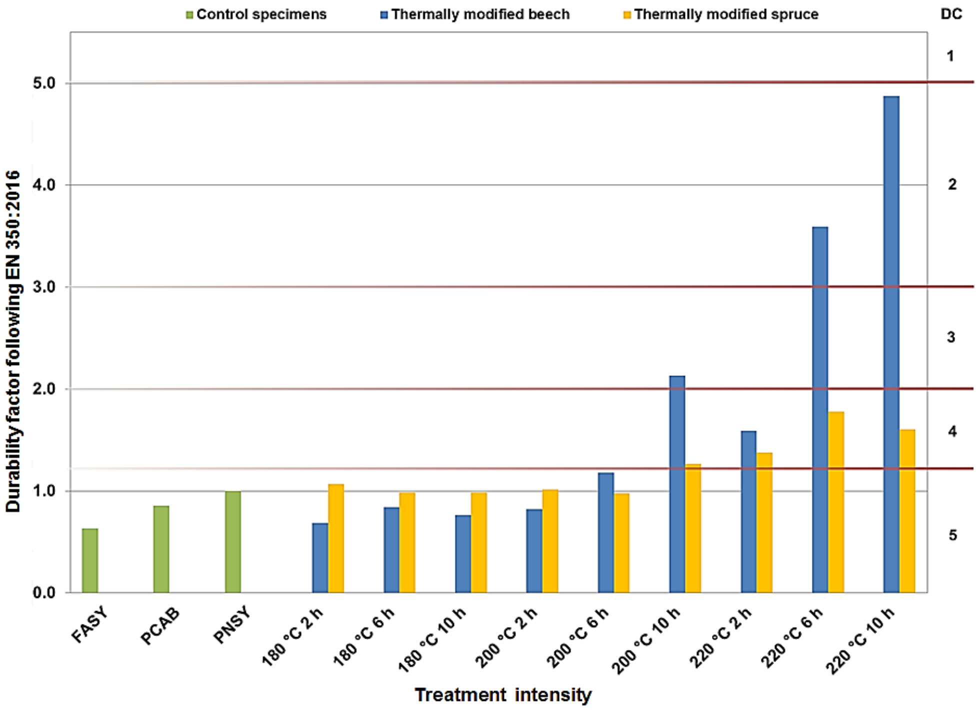

Figure 1: Durability factors and classes (DC) for control specimens and thermally modified beech (n = 12 per treatment intensity) and spruce (n = 10 per treatment intensity) after five years in soil contact

Scots pine was the most resistant of the controls. So these were used for the durability classifications. The DC of the soil contact test following EN 350 (2016) is shown in Figure 1. The modified beech wood of treatment intensities 220 °C for 6 h and 220 °C for 10 h reached DC 2 (durable). Modified spruce achieved DC 4 (slightly durable) at most. Thus, a notable correlation between biological resistance and increasing treatment temperature was shown. For modified spruce, slight improvements to biological durability were made.

Comparative Durability Studies from Field and Laboratory Tests

Tables 2 summarizes the results of the different test areas. Notable differences between the testing methods were obtained. Under laboratory conditions with all test fungi, DC 5 was mainly determined for the beech controls, similar to the in-ground test results. With rising treatment intensity, the modified beech specimens tested with *O. placenta* showed a notable increase in durability from 180 °C for 10 h onwards. Comparisons between the results of the *G. trabeum* and the in-ground field tests showed minor differences for a sample treatment temperature of 180 °C. However, with increasing treatment temperature, the durability of both tests differed by up to two classes. *T. versicolor* showed small to moderate deviations of the DC over all treatment intensities. Remarkable durability differences for spruce wood were found between the laboratory test and the field test for the white rot pathogen *T. versicolor*.

Table 2: Results of biological durability for thermally modified beech and spruce woods from laboratory and in-ground tests

Wood Species – Treatment Intensity		**EN 113 (1996)**						**EN 252 (1990)**	
		Trametes versicolor		*Oligoporus placenta*		*Gloeophyllum trabeum*		Decay Rate	
		ML (%)	DC	ML (%)	DC	ML (%)	DC	DR	DC
European beech (*Fagus sylvatica* L.)	FASY	31.5	4-5	35.4	5	36.4	5v	4.0	5
	180 °C 2 h	28.9	4-5	16.8	4v	31.4	5v	4.0	5
	180 °C 6 h	24.5	4	14.9	4v	18.3	4v	4.0	5
	180 °C 10 h	26.2	4	9.0	2v	21.4	5v	4.0	5
	200 °C 2 h	23.7	4v	5.2	1v	16.2	4v	4.0	5
	200°C 6 h	12.2	3v	2.3	1v	7.9	1-2v	3.7	4
	200 °C 10 h	7.0	2v	1.3	1	1.3	1	2.6	3
	220 °C 2 h	9.7	2v	1.6	1	3.9	1	3.3	4
	220 °C 6 h	6.5	2	1.3	1	1.3	1	1.6	2
	220 °C 10 h	3.9	1	1.0	1	2.3	1	1.1	2
Norway spruce (*Picea abies* (L.) H. Karst.)	PCAB	-	-	-	-	-	-	3.9	5
	180 °C 2 h	7.6	2v	21.2	4	18.9	4	3.8	5
	180 °C 6 h	7.5	2	20.1	4	18.3	4	3.8	5
	180 °C 10 h	6.2	2	17.2	4v	14.3	4v	3.9	5
	200 °C 2 h	4.3	1	14.6	4v	15.5	4v	3.9	5
	200°C 6 h	5.4	1-2	10.6	3-4v	15.0	3-4	3.9	5
	200 °C 10 h	4.4	1-2	5.1	1-2	15.2	3-4	3.7	4
	220 °C 2 h	2.6	1	1.8	1	11.4	3	3.6	4
	220 °C 6 h	1.1	1	1.0	1	2.3	1	2.9	4
	220 °C 10 h	1.0	1	0.5	1	2.6	1	3.3	4

The wood-destroying microorganisms required approximately two years in soil contact until a notable onset of woody substance degradation in modified spruce wood was recorded. Transferred to the incubation period of 16 weeks in the lab test, the assumption can be put forward that this period was not sufficient until a humid environment conducive to wood degradation was created for the thermally modified spruce wood. Due to the hydrophobic character of thermally modified wood, the test fungus required a longer period of time to set the necessary degradation moisture. Investigations by Tausch (2011) with an incubation period of 32 weeks showed that the mass loss after crossing the 16 week incubation period on thermally modified softwood in some cases doubled. This suggested a better DC regarding *T. versicolor*, but it actually turned out to be lower. Some results in this study for the durability classifications of less intensely thermally modified spruce (180 °C for 2 h up to 200 °C for 10 h) were in agreement with findings by other authors. Thus, Metsä-Kortelainen and Viitanen (2009) found a moderate to slight durability (DC 3 to DC 4) for thermally modified spruce from laboratory tests. Compared to lab tests, the durability of the test specimens from the in-ground test was lower for both wood species, which was primarily due to the natural diversity of the organisms living in the soil substrate. Likewise, the climatic conditions and the exposure time were decisive criteria. Similar results were found by various authors (*e.g.* Brischke and Meyer-Veltrup 2016).

CONCLUSIONS

Increased biological durability by thermal modification was determined for the lab test in accordance to EN 113 and for the in-ground test EN 252. Referring to the in-ground test, a notable increase was found from the treatment intensity of 220 °C for 2 h for modified beech wood and from the treatment intensity 220 °C 6 h for modified spruce wood. According to DC in accordance to EN 350, modified beech wood 220 °C 6 h and 220 °C 10 h reached for the in-ground test the durability class 2 (DC 2, durable), modified spruce achieved DC 4 (slightly durable). A conclusion to soft rot or white rot attack in the in-ground test was determined by the quick progression of high decay rates with regard to the controls and lower modified beech wood specimens. By determining the degradation velocities, an initialization phase was found for the highly modified test specimens. For the thermally modified beech wood, *G. trabeum* showed minor relevance, while *T. versicolor* obtained moderate deviations. For spruce wood, notable differences for *T. versicolor* between the lab test and the in-ground field test were found. The comparative investigations between thermally modified wood from the in-ground test and the lab test elucidated that a final assessment of the durability based on laboratory results alone is not realistic without validation under real conditions.

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Appearance of solid wood decking: requirements and assessment

Wolfram Scheiding, Philipp Flade, Katharina Plaschkies, Björn Weiß

Institute for Wood Technology Dresden (IHD), Zellescher Weg 24, 01217 Dresden, Germany
[wolfram.scheiding@ihd-dresden.de; philipp.flade@ihd-dresden.de; katharina.plaschkies@ihd-dresden.de; bjoern.weiss@ihd-dresden.de]

Keywords: aesthetic appearance, assessment, decking, requirements, solid wood

ABSTRACT

Terrace or balcony decking is still the most important exterior application for solid wood compartments made out from modified timber, followed by façade cladding. The total market volume for decking in Germany was estimated in 2013 by 14.5 Mio. m²/a; the share of the market of modified timber had been estimated with 15 % (Langen 2013). Unfortunately, no more recent data are available, but the total market volume and the market share of modified timber should have probably increased.

Although the demand for wooden decking or cladding is increasing continuously, problems and complaints with the appearance arise likewise. The changes in appearance are concerning both uncoated and coated commodities, and often occur already after a few weeks or months. Reasons are often discolouration, which are caused by micro-organisms or result from weathering or chemical reactions. Many technical reports compiled by the authors have shown, that modified timber, particularly thermally modified (TM) wood, is particularly concerned.

Requirements on both technical performance and appearance can result from regulations, standards, but particularly from contractual agreements. Decking from solid wood compartments is currently regulated by standards. In contrast, for decking out of WPC and NFC, the EN 15534, and EAD 190005-00-0402 for "terrace decking kit" are available. However, specific requirements on the aesthetic appearance are not given. A method to assess the appearance of sawn and processed timber is described in prEN 1309-3. However, only assessment criteria for knots and knottiness are given.

Beside other technical functions and properties, like strength, biological durability, or abrasion resistance, the aesthetic appearance is to be considered as essential property or function of decking. On the other side, it is difficult to assess the appearance, since this quantity is not measurable.

For producers, wood traders, and processors it should be important to know the difficulties with appearance and aesthetic function of decking. Proper information to the customer during sales procedure e.g. on ageing and discolouration to be expected, and a reasonable dealing with complaints and claims, will provide to success in business with modified timber.

The paper is dealing with requirements on and assessing of aesthetic/visual appearance and deficiencies of wooden decking, respectively.

INTRODUCTION

Outdoor decking, in particular for terraces and balconies, are an important application for solid wood or wood-based materials. Following wood species or wood products are of a larger market importance:

- Tropical wood species, like Bangkirai, Teak, Garapa, Massaranduba, Ipé,
- impregnated pine of spruce ("green commodities"),
- heartwood of domestic or cultivated softwoods like larch or Douglas fir,
- heartwood of oak, rarer of Black locust,
- thermally modified timber (TMT) and chemically modified timber (CMT),
- hydrophobically (oil, wax) treated timber
- wood-polymer or natural fibre composites (WPC and NFC),
- bamboo scrimber (as well referred to as compressed bamboo or strand woven bamboo).

Due to the conditions in service, decking is to be allocated to use class 3.2, according to EN 335. Here, a risk of attack by wood-decay fungi is given. Therefore, the timber used has to be of a specific natural durability, or to be treated sufficiently by e.g. preservatives, modification, or hydrophobic agents. The resulting biological durability is to be proven by appropriate test methods.

Although the market demand for decking is developing generally positively, increasingly problems arise with microbial discolouration; which frequently occur already a few weeks after installation. Both untreated and coated products are objected by this phenomenon. The authors have compiled many expert reports on this issue.

Beside weathering (abiotic factors) and resulting greying, the changes in appearance are mainly caused by wood-discolouring (wood disfiguring) blue stain and mould fungi, and by aero-terrestrial algae and bacteria.

Since the microbial discolouration often occurs surprisingly early, i.e. in the beginning of the guarantee period, the microbial discolouration is frequently reclaimed – in contrast to the usually accepted greying. Problems and claims due to microbial growth on surfaces which are exposed outdoor are increasing continuously – at least from the perspective of an expert. Four important reasons are seen:

- improved air quality with reduced sulphur concentration (e.g. Rüther 2012),
- increasing consumer need on wooden decking and cladding,
- increasing demand of end users on quality,
- decreasing tolerance of end users against deviations from the expected.

The increase of complaints and claims is objecting obviously as well (indoor) flooring. Discussions with experts have shown, that previously wooden flooring had been appreciated by end users for its natural appearance including characteristics like knots, fibre deviations, or different colours. But, today consumers apply industrial standards.

End users (clients, house owners) apply medium up to high aesthetic demand on terrace and balcony decking, which are particularly high during the first weeks after installation. A discolouration of solid timber within a few weeks or months is often not expected by end users.

EXPERIMENTAL

Typical impairments of visual appearance

Cases of microbial discolouration are mostly wood discolouring fungi, i.e. blue stain and mould fungi, as well as aero-terrestrial algae; the latter are often (but falsely) called as moss (fig. 1). Occasionally occurs growth by lichens, but real moss is seldom found and if, where dust was accumulating. The technical function of decking is usually not or negligible affected by the growth of those microorganisms, irrespective of anti-slip fastness, which can be decreased particularly by algae (Plaschkies *et al.* 2013).

If decking is treated with film-forming coatings, e.g. glazes, weathering can affect cracking or delamination of the coating layer. The open and unprotected areas are greying and getting wet, and are quickly grown by wood-discolouring microorganisms. For thermally modified ash, frequently spotted discolouration is observed (fig. 2); here, obviously the normal greying does not happen in the ovally shaped spots; the reason for this is still unknown. When the heartwood from oak, larch, pine, or Douglas fir gets contact with iron metals and moisture, the so-called iron-tannin-reaction can occur, resulting in a bluish-back discolouration of the wood.

An intensive knottiness can also impair the appearance. However, this is a question of quality grading of the material and strikes already during installation or the approval of the works. Occasionally, maceration is rejected; this is caused by napped appearing wood or cellulose fibres, which peel off from the surface. Greying of wood is a well-known occurrence, which is indeed undesired, but generally accepted. In contrast, cracking, distortion, and discolouration caused by microorganisms are rarely accepted, what is often resulting in complaints. Additionally, two complicating factors are to be considered: One the one hand, the client (end user) is particularly discriminating during the first weeks or months after installation of a new decking; on the other hand, the criticised discolouration occurs in the same time, which is the beginning of the guarantee period. From the perspective of an end user, particular advantages are expected from wood-polymer composites. This is reflected by a high and continuously (2-3 % per year) increasing percentage of this material among decking, although the prices are relatively high (Langen 2013). However, experience of the authors shows that with wood-polymer composites, problems with discolouration and growth by microorganisms also can occur (Plaschkies *et al.* 2013).

Figure 1: Thermally modified ash with discolouration by blue stain and mould

Figure 2: Spotted pattern of a decking from thermally modified ash

Requirements

Decking coverings for terrace, balcony, platform etc. made out of wood and wood-based materials are currently not regulated by European standards. Normative requirements on biological durability against wood-decay fungi are determined in EN 460. This standard forms a link between use (formerly hazard) classes and the required durability (currently this standard is under revision by CEN/TC 38 WG 28). Furthermore, requirements on durability for load-bearing or non-loadbearing components may result from national standards.

Following properties can be relevant for decking applications:
- biological durability against wood-decay fungi
- static bending strength, load-bearing capacity against point loads
- dynamic (impact) bending strength
- surface hardness (Brinell)
- tendency for crack formation
- tendency for discolouration due to growth of microorganisms
- suitability for surface treatment

Visual appearance as essential product property

Generally, a product has to fulfil its essential functions during entire service life. For construction products, but as well for decking, these are usually technical functions or achievements. However, there are some other construction products at which the appearance is as well to be considered an essential function. For exteriors, these are e.g. windows, cladding, or decking; for interiors, these are flooring, cladding, or panelling.

When the appearance is impaired more than acceptable or reasonable, in principle the end of the aesthetic service life is reached. This point in time is usually reached earlier than the end of technical service life.

Expectations

The expectation of a client, building owner, or consumer often results from viewing material samples, example areas shown indoor or outdoor, reference objects as well as documents and photos on print media (brochures) and electronic media (websites). On Photos is shown usually the as-new condition, which will be changing considerably already within few weeks or months after installation, as far as the surface is not protected, e.g. by terrace oils or other suitable coatings.

As a further problem, distinct wording of suppliers is vague and can be understood differently by the contract parties. Examples are e.g. "valuable", "precious patina", "long-lasting", "weather resistant", or "durable".

The expectations of consumers on modified timber are in many cases particularly high, compared to those on "common" timber. This can be explained by the following reasons:

- modified timber is considered as technically enhanced,
- all properties, including appearance, are expected as to be durable,
- less practical experience, compared to common wood,
- better visibility (higher contrast) of colour changes, e.g. greying of dark-brown TMT or dark biofilms on bright (acetylated) CMT,
- accelerated greying TMT, compared to common wood species,
- common surface coatings (oil tec.) not always appropriate to modified timber.

Assessment

It is generally difficult to assess visual (aesthetic) defects or defects in appearance. Always other functions or possibly defects and the context with adjacent areas of the building object must be considered comprehensively. Hence, an assessment by an expert in situ is necessary (or strongly recommended) in any single case. However, there are some general rules to assess deviations or defects in appearance. The assessment shall be guided by the weight of appearance, comparing to other functions, and by the degree of the impairment of appearance (Ertl *et al.* 2017). Generally, one can distinguish between a bagatelle, as deviation to be accepted, and a defect, as unacceptable deviation which has to be remediated. A bagatelle affects the aesthetic appearance not or only negligible. Ertl *et al.* (2017) proposed that an assessment should base on general rules:

- visual irregularities shall be always remediated, if possible easily and cheap,
- no contractual agreements on visual appearance were made,
- it should be checked, whether a bagatelle or an impairment is prevailing.

Beside the differentiation between technical functionality and appearance, the assessment can be easier if requirements are subdivided into expectation or quality levels, e.g. low, normal, high, and premium (e.g. Pitt 2016). The level results particularly from the type of client, the expectations on quality, and the quality level of the entire property or building object. The difficulties in assessing the appearance are often caused by the following reasons:

- the client (non-professional) was not enlightened sufficiently about normal changes in appearance which must be accepted;
- wrong expectations had been raised (unintentionally) with the client, e.g. by the advertisement of the supplier;
- the client did not or insufficiently communicate his expectations;
- the term "nice" is a subjective one, difficult to define and not measurable;
- emotions decide considerably about the client´s acceptance.

For experts it is often difficult to assess, whether the construction product still fulfils its aesthetic function, since in many cases, no normative requirements, other technical rules, or concrete contractual agreements are available as reference.

It should be considered, that the visual appearance results from many single characteristics, where only some can be assessed objectively. But, the overall aesthetic impression is a subjective category, thus an assessment is possible only for the individual case.

Following considerations could be helpful in the case of complaint, claim, or lawsuit:

1. Which changes result from weathering and normal use?
2. Did the aesthetic demand change while exposure to weather and wear?
3. What is the aesthetic service life (considering cleaning and maintenance)?
4. Is the current condition accepted?
5. Was the appearance agreed explicitly or is to be considered as agreed implicitly?
6. Does the appearance deviate from the agreed or expected one?
7. Is the deviation essential or exceeds an acceptable limit?
8. What are the reasons for the deviations (quality of material and installation, weathering, wear)?

If – as often – no clear criteria for the appearance were agreed, it is very difficult to define what is a "usual appearance" or a "usual quality". However, the demands must be based on concrete facts. Criteria which can be used to assess a terrace, balcony, or platform decking are listed in table 1. The investigation should be performed by the expert with daylight, from a standing-up perspective, from usual viewing positions, and when the surface is dry.

Table 1: Criteria (characteristics) to assess the appearance of decking

Assessment in as-new condition	**Assessment in use condition**
single decking boards:	Shadowing (e.g. by building, trees)
wood species	covering by objects (furniture, planters)
Texture (grain/annual ring pattern)	mechanical wearing (abrasion)
knottiness (number, size, behaviour)	weathering (greying, erosion)
size (cross-section, length)	maintenance condition
shape (grooved, smooth)	cleaning condition (pollution)
surface treatment (oil, glaze)	deformations
	gap width (intermediately, to adjacent areas)
decking (entire area):	crack and splinter formation
size and shape of entire area	maceration (detaching of fibres)
lateral distances	discolouration due to reaction with metals
type of abutting joints	fouling by wood-decay fungi
direction of installation	discolouration by blue stain and mould
type of fixing (visible, not visible)	growth by aero-terrestrial algae
usual perspective (user)	
context to building and premises	

CONCLUSIONS

Visual or aesthetic appearance of decking for terrace, balcony, platform and others is an essential product property. The assessment of visual or aesthetic appearance is usually a task for experts, which is required for cases of complaints, claims, or lawsuits. To prevent them, as well producers, suppliers, and traders should consider the importance of appearance and its changes due to weathering and wearing.

An important factor to prevent complaints and claims is to communicate properly which changes in appearance are normal and thus to be expected and to be accepted. Furthermore, the consumer should be clearly informed about his own responsibilities, particularly to ensure an appropriate maintenance.

Since the assessment of changes in appearance is difficult, experts are requested which provide a neutral and technically based investigation, and to ensure an objective and fair discussion between the parties.

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Monitoring the performance of Accoya® in different applications

René Klaassen[1], Bôke Tjeerdsma[2], René Hillebrink[3]

[1]SHR, Nieuwe Kanaal 9^b, NL-6709 PA, Wageningen [email: r.klaassen@shr.nl]
[2]SHR, Nieuwe Kanaal 9^b, NL-6709 PA, Wageningen [email: b.tjeerdsma@shr.nl]
[3]SHR, Nieuwe Kanaal 9^b, NL-6709 PA, Wageningen [email: r.hillebrink@shr.nl]

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ABSTRACT

More than 10 years ago, industrial production of acetylated radiata pine started under the trade name Accoya in the Netherlands. This early industrial production of Accoya was used in different building applications above ground as well as in ground and water contact. Over these past 10 years a tremendous amount of real life experiences with Accoya in commercial applications has been obtained. In order to learn more about the long term performance of the acetylated radiata pine in these applications, projects were visited and the quality of the acetylated radiata pine was inspected. Most projects selected were older than 5 years, without or with limited maintenance. In total 17 projects were inspected including acetylated wooden doors, windows, window frames, claddings, and sheet pilings. This paper summarizes the results of the inspections in terms of functionality, maintenance frequency, coating quality, moisture content, smell, decay and corrosion. Furthermore the results are discussed in relation to the special technological properties of Accoya.

INTRODUCTION

The process of acetylation improves the wood quality by a reaction of acetic anhydride with the cell wall. The wood is fully impregnated and in the reaction that takes place one molecule acetic acid is attached to the cell wall and the other one is released in the cell lumen. Because of this reaction the cell wall swells, the wood density and resistance against microbiological degradation increases and the equilibrium moisture content and shrinkage behaviour decreases. The degree of improvement of these properties and the removal of the remaining acetic acid, depends on the intensity and quality of the process of acetylation (Hill 2006, Tjeerdsma and Bongers 2009, Bongers *et al.* 2013).

Accsys in Arnhem produces acetylated timber under the brand name Accoya and their timber is used in joinery and a variety of outdoor building constructions. Their timber is highly dimensionally stable and has a high resistance against fungal decay. In order to avoid corrosion with metal parts or any emission of acetic acid, the industrial processing is optimised in order to remove as much of the remaining acetic acid as possible.

Although the industrial production of Accoya started in 2007, pilot projects were established even earlier and especially during the first production years their process was further improved, resulting in a more homogeneous treatment, a more homogeneous moisture content of the treated timber and a low concentration of residual acetic acid of below 1%.

In order to monitor the performance of Accoya in different applications, several projects were investigated and special attention was given to those properties which were affected by the process of acetylation.

SELECTION OF THE PROJECTS

In cooperation with Accsys, the Dutch joinery industry, the Dutch paint producers and on the basis of the internal SHR database, a selection of projects was made and visited (Table 1). In the majority of the projects, the modified timber was used as painted joinery (windows, window frames, doors, door frames) and no maintenance was performed during the years of use. Two projects consisted of unpainted timber (joinery claddings). Furthermore, there were two large flooring projects and several projects with outdoor constructions (canal linings with pile planking).

Table 1: information of the projects inspected, unless otherwise given the projects are newly built and without maintenance

Building year	location	Construction type	Use	Ownership
2000	Flevoland	Sheet piling	Pile planking	Government
2007	Den Haag	Family houses	joinery	Private
2007	Den Haag	Family houses	joinery[b]	Housing association
2007	Voorthuizen	Canal wall protection	Pile planking	Government
2008	Amsterdam	Flat, 5 stocks	joinery[a]	Housing association
2008	Wageningen	Office building	Window frames[b]	University
2008	Wageningen	Office building	claddings[b]	University
2009	Amsterdam	8 historical apartments	joinery[a]	Housing association
2010	Amsterdam	Restaurant	joinery[a]	Private
2012	Wageningen	58 family houses	joinery[a]	Housing association
2012	Den Bosch	65 Family houses	joinery[a]	Housing association
2012	Amsterdam	Flat, 16 stocks	Unpainted joinery	
2012	Wageningen	124 family houses	joinery[a]	Housing association
2012	Oss	shelter	joinery[a]	Housing association
2014	Almere	Single house	joinery	Private
2015	Assen	Outdoor Cycle track	Floor	Government
2016	Apeldoorn	Indoor Cycle track	floor	Government

[a] renovation projects [b] projects with periodic maintenance applied

METHOD

In the period March 2017 to May 2018, all project except the cycle tracks were visited and visually inspected with attention for functionality, cracks, corrosion, fungi (blue stain, decay), smell, adhesion (dirt, algae, mosses, fungi), distortion, glued quality (corner joints, finger joints / lamellae, marking), paint quality (loss of adhesion, blistering, discoloration) and crystallisation. If relevant, moisture content measurements were done using a capacitive moisture meter (Brookhuis, FMW, wood density 550 kg/m³). The found status of the timber products was discussed with reflection towards design, orientation and use. Both cycle tracks were visited in the building phase and special attention was given to cracks and release of odour.

RESULTS AND DISCUSSION

In this section the results of the inspections are discussed as general trends over all the projects. Several main trends can be distinguished in the use of Accoya timber related to: increased dimensional stability; residual acetic acid; glue-ability, crack formation; changed moisture behaviour; decay.

The impact of strongly reduced shrinkage and swelling on the material and product behaviour

Shrinkage and swelling of the wood as a result of changing surrounding humidity is strongly reduced by the acetylation treatment. The impact of this dimensional stability was noticeable in all projects by the well-functioning and non-deformed windows and doors. The quality of the 6 to 10 years old paint layers in the projects was still good and meeting the requirements, therefore showing a painted surface without cracks or blistering. Because different paint products with diverse properties were used, a wide range of paint surface degradation was recorded with respect to gloss and chalking.

The high dimensional stability prohibits the timber to react in its usual way. Untreated wood shows a higher shrinking and swelling of latewood compared to the early wood. This results in a visible print of the timber pattern in the paint layer. As this effect is absent in dimensionally stable Accoya, the wood surface stays extremely flat and gives the timber often an almost plastic alike appearance.

On both long sides in the 250 m indoor cycle track (Figure 1), shutters are included for opening of the track to enable large equipment to enter the centre of the court. In summer the seams at both ends of the shutter are about 10 mm and in the winter they are 7 mm smaller (Figure 2). Calculated with respect to the length of the track, this means a longitudinal shrinkage of about 0.01% , which is ten times less compared to non-treated wood. The moisture content of the modified wood under these indoor track conditions varies in the summer and winter period between 3 and 8%.

Figure 1: Cycle track with on the right an opening where the shutter is removed.

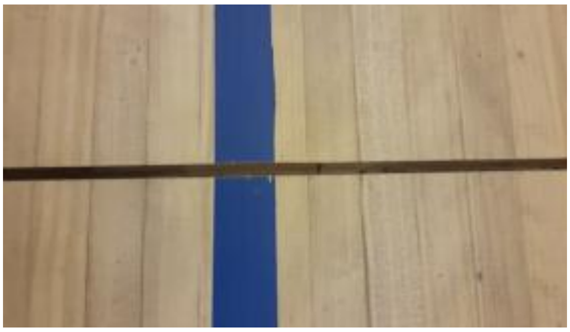

Figure 2: Interface of the shutter and the cycle track, showing the size of the seams in the winter.

Residual acetic acid in the timber

Inspection of some of the oldest projects, revealed some emission of acetic acid. Just by removing the paint layer or drilling a hole, the typical smell was detectible. In the more recent projects no clear acetic acid smell was recorded. During the construction of the new indoor cycle track more than 90 m³ non-coated acetylated timber was used under indoor conditions with limited ventilation. In the first days directly after installation, only a light acetic acid odour was observed by a limited number of persons of the test team, despite this huge amount of acetylated timber used under indoor conditions. The analyses showed that the residual acetic acid in the wood was between 0,1 and 0,3%.

In some of the projects (Den Haag 2007, Wageningen 2012 and Almere 2014) heavy corrosion was seen. In all of these projects, the corrosion was related to extreme water load and the use of non-corrosion resistant metals. In Den Haag the joinery was stored unprotected for a longer period. The high corrosion in the sheet doors, which open to the outside, in the 2012 Wageningen project was caused by use and construction. Frequently the sheet doors stood open for a longer time and the connection between the metal locks and the wooden part acted as a funnel causing water storages around the metal door clasp (Figure 3). In case of joinery in the Almere project, problems with condensation, causes water storage around the metal locks (Figure 4).

In all other projects the water load was to a much lower extent and although often non-corrosion resistant metals were used, no corrosion was seen, not even in the unpainted joinery.

Based on our findings we concluded that heavy water load is the main feature for causing metal corrosion in acetylated joinery timber rather than a general material characteristic of Accoya itself.

Figure 3: Sheet door which stood frequently open causing water accumulation in the lock resulting in corrosion on the metal parts.

Figure: 4 Window with high and long term condensation causing corrosion on the metal parts.

Effect of residual acetic acid on paint layers was found insignificant. During none of the project visits, loss of adhesion of paint layers was seen in relation to residual acetic acid. Crystallization as a reaction of residual acetic with environmental substrates could take place and was rarely found in and through paint layers and only in connection with high water loads e.g. open joinery connections (Figure 5 and 6). Based on these findings it can be concluded that residual acetic acid does not have a negative effect on the quality of the paint layers except in situations with a high water load and moisture transport through the timber. In these high water load situations already low remaining acetic acid concentration (e.g. < 0.3%) can have an effect on paint performance.

Figure 5: Joinery with small humps near the corner.

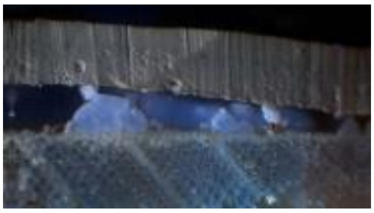

Figure 6: Microscopic image of crystallization between the flow coat and top coating layer.

Figure 7: Beam in cycle track Assen with a removed shallow peel which was a result of a drying crack.

Glue lines of laminated timber

In none of the projects visited, structural delamination or open corners connections were found. This shows the high potential of producing durable glued connections and well performing laminated beams with acetylated wood.

Cracks

Cracks caused by or during the acetylation treatment were not seen in any of the projects. For both cycle tracks some of the delivered timber beams during the building phase, included drying cracks resulting in shallow thin peels. The number of these cracks did not increase in time, after the timber was included under tension in a curved position (Figure 7).
In joinery no cracks were seen other than those related to the production (e.g. timber was split because of the use of too high force or the use of too narrow connecting parts).

Moisture content

Because of the acetylation treatment the timber has a low equilibrium moisture content. In exterior joinery without exceptional local water load caused by open connections or internal water condensation, the recorded moisture content normally was between 2.5 and 4.5%. However the moisture content can be much higher near local moisture load caused by damage, resulting in wet conditions of the acetylated wood for longer periods. The acetylated wooden cell wall is more hydrophobic leading to a disturbed transport or diffusion of water inside the wood. This disturbed transport of water causes a slow release of moisture and water accumulation in wood, leading to slower drying characteristic of acetylated wood compared to untreated wood. Although long term high moisture content did not result in decay or substantial swelling, it can give some unwanted side effects. In claddings (Wageningen 2008) with a high water load because of unsealed upper cross surfaces, resulted in mould and moss growth on the paint layer (Figure 8).

Figure 8: Moss and fungal growth on paint layer of wet timber.

Figure 9: Window frame with high moisture content causing paint damage.

Window frames which were not handled properly in the building phase (Wageningen 2008) caused deep penetration of free water through the end grain into the cell lumen of the timber. During the first several years, these high moisture contents, combined with solar exposure caused severe loss of adhesion of the paint. Only after several attempts to repaint the window frames, a stable situation was reached in 2017 (Figure 9).

In case of joinery it is concluded that the fast water uptake through the end grain surfaces, leading to free water in the wood, should be avoided and special methods or maintenance instructions should be developed in order to remove free water in acetylated timber building products.

Unpainted exterior joinery

Inspection of a 6 year old project with un-coated joinery and cladding revealed a clean and grey impression of the wood surface (Amsterdam 2012, Figure 10, 14). Caused by UV radiation over a period of 6 years, the fibres on the exposed wood surface of the joinery were only degraded in an outside layer with a thickness of several cell layers deep. However, depending on the degree of exposure, the surface was darker because of dirt adhesion and mould growth. On locations where the wood was exposed for longer time to high relative humidity, additional moss and algae growth and more extensive mould discoloration was seen (Figure 11). Local differences in discoloration were on some places quite extensive resulting from grooves in the joinery itself or expended materials like bricklayers (Figure 12). Furthermore in some cases the blocks between the finger joints react differently on exterior exposure (Figure 10). It is unclear whether small moisture content differences or the timber quality itself is causing this effect.

Figure 10: Unpainted joinery, clean, partly homogeneously discoloured, partly heterogeneously e.g. door.

Figure 11: Unpainted joinery with lichen on moisture areas.

Figure 12: differences in discolorations and mould growth.

After six years in use it is remarkable that the indoor surface of the joinery is unaffected by exposure and use (Figure 12, 13, 15). The inspected surface of the indoor surface of the timber was clean and whitish. Only on a limited number of locations and always near connections brown discolorations were seen (Figure 13). It is suggested that this discoloration is caused by water transfer from outside inwards.

Opening and closing of the doors and windows as well as the wind and water tightness of the joinery was never a problem. Only in the wet season the consulted residents mentioned that the inside of the turning elements were sometimes somewhat humid. It was not possible to verify this because the inspection was done after a dry period of several days and the moisture content of all the joinery was between 3.5 and 4.5%. No signals of corroding locks were found anywhere in the building, despite the fact that the joinery was unprotected against direct water exposure and assumed water transfer through the wood.

Figure 13: Clean inside timber surface with some brown discolorations.

Figure 14: Clean and homogeneous discoloration (greying).

Figure 15: Clean joinery and non-corroded locks.

Decay

In none of the projects without soil contact, clear signs of decay were observed and under more extreme conditions like in the application of sheet piling (Flevoland 2000 and Voorthuizen 2010), after 10 to 15 years of exposure, no significant decay appeared and the planks were still hard, the construction was coherent and still functioning.

CONCLUSIONS

Based on all the results of the project visits we conclude that the use of acetylated wood increases the lifetime of timber products and decreases the intensity of maintenance. However, special attention is needed to avoid fast water uptake in outdoor as well as in indoor (condensation) conditions and to develop techniques that can accelerate the removal of accumulated water in the wood.

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Performance of chemically modified wood under marine conditions during nine years of exposure

Christian Brischke[1], Antje Gellerich[2], André Klüppel[3] and Holger Militz[4]

[1]University of Goettingen, Wood Biology and Wood Products, Buesgenweg 4,
D-37077 Goettingen [email: christian.brischke@uni-goettingen.de]
[2] University of Applied Sciences Merseburg, Eberhard-Leibnitz-Str. 2,
D-06217 Merseburg [email: antje.gellerich@hs-merseburg.de]
[3]University of Goettingen, Wood Biology and Wood Products, Buesgenweg 4,
D-37077 Goettingen [email: Andre.Klueppel@forst.uni-goettingen.de]
[4]University of Goettingen, Wood Biology and Wood Products, Buesgenweg 4,
D-37077 Goettingen [email: hmilitz@gwdg.de]

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ABSTRACT

Wood and wood products used for marine applications are exposed to an extremely harsh environment. Most Europe-grown wood species such as Scots pine (*Pinus sylvestris*) or European beech (*Fagus sylvatica*) are not durable against attack by marine organisms. To protect susceptible wood species, chemical wood modification might be an alternative. This study focused therefore on impregnation modification with thermosetting resins, acetylated (Accoya) and silica containing wood (TEOS) and was started in 2008. Results after nine years of exposure at the Danish test site Hejlsminde are presented. Acetylation and modification with thermosetting resins at higher weight percent gains (WPGs) increased the durability against shipworm significantly. In contrast, the DMDHEU, melamine resin and phenol resin treated wood at lower concentrations showed only a poor resistance against shipworm decay and were severely decayed after two to three years of exposure. The results clearly indicated that the crucial factor for a resin treatment to protect wood against shipworms is the amount of resin deposited in the cell wall and the curing conditions. In summary, modified wood showed high potential for use in sea water contact. However, for a deeper understanding of the protection mechanisms further studies are needed to investigate the influence of process and curing parameters as well as the distribution of chemicals. To assess the suitability of these treatments for constructions in the marine environment, such as groynes, jetties and sea bridges an upscaling to full size dimensions will be necessary in the future and has been initiated.

INTRODUCTION

Since millennia wood is a traditional building material in the marine environment. Wood and wood products used for marine applications are exposed to an extremely harsh environment. Besides a more or less permanent wetting, wooden structures are submitted to a wide range of degrading organisms including different bacteria, decay fungi and marine borers such as shipworms and gribble. Most of the home growing wood species are not durable against attack by marine organisms (EN 350, 2016). Therefore, some very durable wood species, in particular tropical species, and a wide range of differently preservative treated timbers were used in the last decades for groins, jetties or sea bridges and acceptable service lives were achieved with wooden structures all around the globe.

Today, the situation in Europe is somewhat different: Currently, no wood preservative is approved for application in use class 5 (UC 5, EN 335, 2013), i.e. in contact with sea water.

Many highly effective preservatives have been banned for reasons of ecotoxicity and because of being harmful to human health. The use of tropical wood species is increasingly restricted since their production is associated with illegal logging, deforestation, and socio-political problems in the respective origin countries. The costs for tropical timbers are on average three times higher compared to home-grown Scots pine (Saathoff *et al.* 2010). Lesser durable tropical species and plantation grown timber could not compete with material from original stands. In search of affordable substitute products some Europe-grown wood species such as Black locust (*Robinia pseudoacacia*), Sweet chestnut (*Castanea sativa*), and English oak (*Quercus robur*) were used for instance for groins, but led to numerous premature failures. Even on the coastline of the Baltic Sea, where shipworm attack has never been a significant problem in the past, and where even the moderately durable Scots pine heartwood was successfully used, the number of damages on groins, dolphins, fascines, jetties, and revetments increased dramatically (Saathoff *et al.* 2010, Lippert *et al.* 2017). Due to an increase in salinity, temperature or adaption of shipworms to lower salinities-temperature combinations, nowadays also shipworms spread within the Baltic Sea and led to severe problems and significant economic damages in Denmark, Germany, Poland, and Southern Sweden. As a consequence of lacking sufficiently durable alternatives made from wood marine structures are recently often built from other materials such as concrete, steel, and polymers – even though the latter suffer from the harsh environment as well – in particular due to corrosion and sand abrasion.

To protect susceptible wood species against degradation in the marine environment, wood modification might be an alternative. Wood modification systems are non-toxic and do not release toxic substances during service life (Hill 2011). Previous studies by Klüppel *et al.* (2012), Slevin *et al.* (2015) and Janus *et al.* (2017) showed the potential of differently modified timber to withstand the attack of marine borers. Therefore, different wood modification treatments were investigated within this study to determine their resistance against shipworms under field conditions. The study focused on impregnation modification with thermosetting resins, acetylated and silica containing wood. The study was started in 2008 (Klüppel *et al.* 2012) and results after nine years of exposure are presented.

EXPERIMENTAL

Treatment of wood

All treatments investigated in this study were applied on Scots pine sapwood (*Pinus sylvestris* L.) except for acetylation, which was applied to Radiata pine (*Pinus radiata* D. Don). An overview of all specimens is given in Table 1. Boards of Accoya® wood and untreated Radiata pine were provided by Accsys in February 2008. DMDHEU treated boards were produced in an industrial scale process and provided by BASF (Table 2). Modification with MMF, PF and TEOS were carried out in laboratory scale and pilot plant processes (Table 2).

Table 1: Number of specimens and installation date of tested materials

Treatment	Number of specimens	Installation date
Untreated reference Scots pine sapwood	10	2008
Untreated reference Radiata pine	10	2008
CC, 0.6% conc.	10	2008
CC, 2.5% conc.	10	2008
Acetylation (Accoya, Accsys)	10	2008
DMDHEU (Belmadur, BASF)	7	2008
Methylated melamine formaldehyde resin (MMF, Madurit MW 840/75WA, INEOS melamines)	10	2008
Phenol formaldehyde resin (PF, Phenodur PR 635/78WA, Allnex)	10	2010
Tetra-ethoxy-ortho silane (TEOS, Dynasilan A, Evonik Industries)	10	2008

Table 2: Overview of treatments with respective concentration of the impregnation solution, resulting WPG and curing conditions

Treatment	Concentration	Approximate mean WPG/retention	Curing conditions
MMF	10%	10%	Kiln dryer pilot plant (mild)
MMF	25%	25%	Oven, dried & cured simultaneously
PF	25%	35%	Oven, specimens wrapped in PET for curing & subsequently dried (wet curing)
TEOS		25%	Applied in sol state
DMDHEU	0.8M		Semi-industrial scale at BASF (Ludwigshafen, Germany)
DMDHEU	1.3M		
DMDHEU	2.3M		
Acetylation (Accoya wood)		>20%	Accoya® boards produced & provided by Accsys (Arnhem, The Netherlands)
CC	0.6%	3.5 kg/m³	-
CC	2.5%	15 kg/m³	-

Preservative treated reference specimens were treated with acid copper chromate composed of 30% (m/m) CuO and 70% (m/m) CrO_3. Concentrations (Table 2) of the preservative solutions were chosen to result in retention of copper and chromium comparable to the reference treatments suggested by the European standard EN 275 (1992). The preservative treated specimens were stored at room temperature for eight weeks to ensure fixation. After treatment the WPG (Weight Percent Gain) and the retention of wood preservative were determined (Table 2). After treatment, the specimens (200 x 75 x 25 mm³) were prepared with a hole of 16 mm in diameter in the middle and attached to ladder-like racks. Plastic tubes of 25 mm length served as spacers between the specimens.

Test site and inspection of specimens

The racks were exposed in the Baltic Sea (Hejlsminde, Denmark; 55° 21’ N, 9° 36’ E) at 2…4 m below medium high tide. Salinity at the test site ranged between 15 PSU and 25 PSU (practical salinity unit; corresponding to 1.5…2.5%). The water temperature varied between 0…5°C in January and 20…25°C in August. The exposure started in May 2008. For inspection, fouling organisms were carefully removed with a scraper and the specimens were x-rayed and reinstalled in the water. Each specimen was rated according to EN 275 (Table 3, Figure 1). Five new untreated controls of Scots pine sapwood were exposed each year.

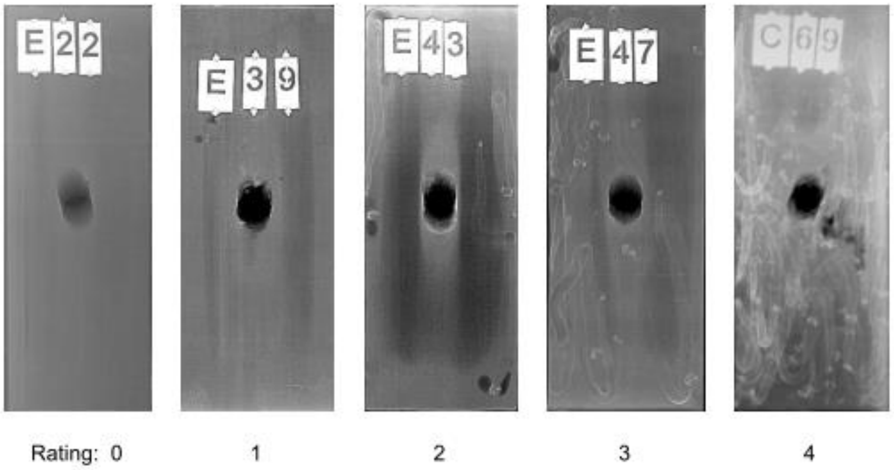

Figure 1: Example of grading shipworm attacks as they appear on the x-ray film

Table 3: Rating scheme for attack by teredinids according to EN 275 (1992)

Rating	Classification	Condition and appearance of test specimen on the x-ray film
0	No attack	No sign of attack
1	Slight attack	Single or a few scattered tunnels covering not more than 15% of the area of the specimen
2	Moderate attack	Tunnels covering not more than about 25% of the area of the test specimen
3	Severe attack	Tunnels covering between 25% and 50% of the area of the specimen
4	Failure	Tunnels covering more than 50% of the area of the specimen

The durability of the investigated materials was determined according to EN 350 (2016). The durability classification was based on the calculation of x-values (Eqn. 1) as specified in Table 4.

$$x - value = \frac{average\ lifetime\ of\ test\ specimens}{average\ lifetime\ of\ untreated\ reference\ test\ specimens} \qquad (1)$$

In addition, the decay rate v was calculated according to Eqn. 2 for comparing variation and severity of attack by marine borers of all materials.

$$v_{mean} = \frac{\sum_i^n v_i}{n} = \frac{\sum_i^n \frac{R}{t}}{n} \qquad (2)$$

v_{mean}: mean decay rate of specimens [a^{-1}]; v_i: decay rate of single specimen [a^{-1}]; R: decay rating according to EN 275 (1992); t: exposure time [a]; n: number of replicate specimens.

Table 4: Classes of durability against marine organisms based on tests according to EN 275 (1992)

Durability class	Description	x-value
D	Durable	$x > 5$
M	Moderately durable	$3 < x \leq 5$
S	Not durable	$x \leq 3$

RESULTS AND DISCUSSION

After nine years of exposure, specimens were exclusively attacked by shipworms; no limnoriids were observed. The shipworm attack of the Scots pine sapwood controls was extensive. Specimens were always destroyed within one year of exposure with the exception of the season 2012. Between the evaluation in 2012 and 2013 they were rated in class 3 (severely attacked) and were completely destroyed after two years of exposure. The untreated Radiata pine samples were also destroyed within one year of exposure. Infestation of reference preservative treated specimens with low concentration (0.6%) started in the third year (see Figure 2) and progressed very fast so that all specimens were destroyed after six years. One of the ten reference specimens impregnated with 2.5% acid copper chromate was attacked by a single individual in the fourth year. After nine years of exposure, three specimens were slightly attacked (Figure 3). It was assumed that during the field trial acid copper chromate leached from the wood (Klüppel *et al.* 2015). This leaching effect was especially significant for the lower initial concentration.

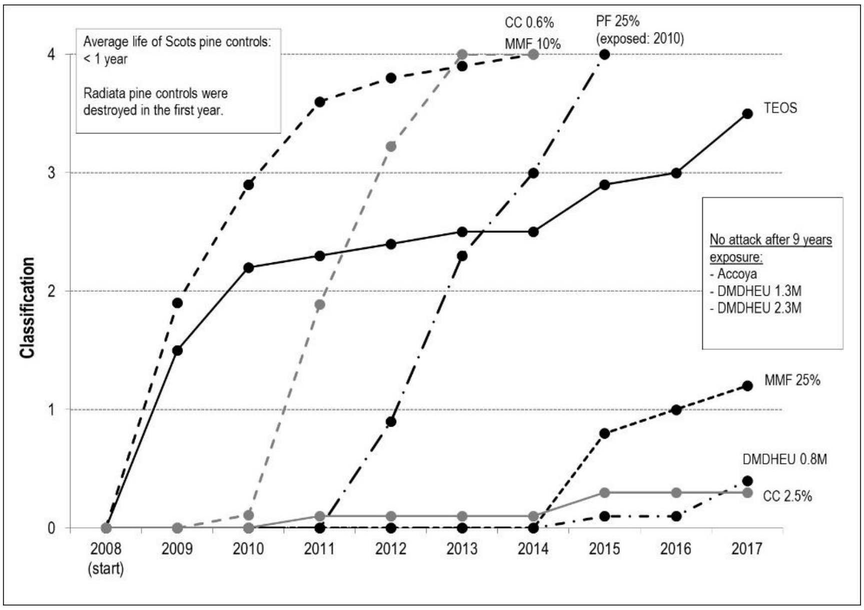

Figure 2: Classification of attack by teredinids according to EN 275 (1992) during nine years of exposure in Hejlsminde, Denmark (CC = copper chromium preservative, DMDHEU = 1,3-dimethylol-4,5-dihydroxyethyleneurea, TEOS = silane, PF = phenol formaldehyde, MMF = melamine formaldehyde)

The Accoya® Radiata pine specimens showed no signs of decay and were ranked as 0 (sound) after nine years of exposure. The specimens were commercially produced with an acetyl content higher than 20%. Acetylated wood specimens with high acetylation levels showed also high resistance against marine borers in other studies (Westin *et al.* 2006, Rowell 2014, Westin *et al.* 2016). The MMF 10% and PF 25% treated wood showed only a poor resistance against shipworm decay and were severely decayed after two and three years of exposure (Figure 3). The MMF 25% impregnated wood specimens showed a better resistance. After six years of exposure, the samples were not decayed and showed no signs of shipworm attack. The infestation started after seven years of exposure (Figure 3) and the samples were ranked between 0 and 3. Westin *et al.* (2006 and 2016) described also differences in resistance of MMF modified wood depending on the weight percent gain (WPG). The 0.8M DMDHEU modified samples showed signs of decay after nine years of exposure. Three specimens were ranked as 1. DMDHEU 1.3M and 2.3M showed no signs of decay after nine years of exposure (Figure 2). The results indicated that the crucial factor for a resin treatment to protect wood against shipworms is the amount of resin deposited in the cell wall and the curing conditions. The importance of curing conditions was also shown for PF-treated specimens which exhibited a poor resistance in the field test against shipworms but performed distinctly better in a laboratory test against *Limnoria quadripunctata* depending on the dry and wet curing conditions (Klüppel *et al.* 2015).

Different established theories related to the protection mechanisms of modified wood against wood destroying organisms were published within the last years. In case of wood destroying fungi that degrade wood cells via oxidative and enzymatic activities the unavailability of easily accessible nutrients, enzyme non-recognition, micropore blocking and moisture exclusion through OH-group blocking/ reduction as well as reduction in void volume are the main principles of action (Hill 2006, Ringman *et al.* 2014). Shipworms digest wood particles with the aid of bacterial endosymbionts in their digestive system which produce enzymes that depolymerize cellulose (Betcher *et al.* 2012; Lippert *et al.* 2017). Due to these similar enzymatic activities it might be assumed that the protection theories of modified wood against shipworms are similar to those against wood destroying fungi. Different protection mechanisms against shipworm decay for acetylated wood and agents polymerizing in the cell wall like MMF, PF and DMDHEU are discussed in literature such as pore size reduction and enzyme non-recognition of the chemically altered wood polymers (Westin *et al.* 2006, Klüppel *et al.* 2015). A major effect might be the interference with the substrate specific binding of the enzyme. A similar effect regarding the modification of cell wall polymers and prevention of cellulose digestion was assumed for the resistance of DMDHEU modified wood against *Limnoria* (Borges *et al.* 2004). Klüppel *et al.* (2015) found also that modifications that prevented infestation by shipworms in the field trial were also particularly effective against *Limnoria quadripunctata* in laboratory tests. However, the protection mechanism and influence factors are not fully investigated and understood.

Specimens modified with TEOS were considerably attacked in the first two seasons. The deviation of early attack was high. Within the first year of exposure, the different wood specimens were ranked between 0 and 3. After nine years of exposure most of the specimens were strongly attacked and ranked as 4, but single specimens showed less infestation and were ranked in class 2. The effectiveness of the treatment might be depending on the distribution of the chemical, the silica's molecular structure, curing (precipitation) and hardness, comparable with the effect of the high silica content in natural durable tropical wood species (Eaton and Hale 1993). The protection mechanism might be related by mechanical effects of the treatment such as blunting of rasping shells and gribble mandibles of the shipworm or disruption of the gut by sharp-edged particles of the substrate (Cookson *et al.* 2007, Scown *et al.* 2001).

Durability classes (Table 5) were determined for the tested material according to EN 350 (2016). Most treatments were classified 'durable' (D) against attack by marine organisms. Treatments with lower WPGs and retention levels were classified as 'moderately durable' (M). However, the deviation particularly of early attack of specimens was high within single treatments such as TEOS, which is to some extent masked by durability classes that did not show the high deviation between the specimens within one treatment. Therefore, also the decay rate was determined (Table 5). Untreated Scots pine sapwood and Radiata pine showed the maximum decay rate of 4.00 a^{-1}, that means specimens failed within one year of exposure. The decay rate showed a high variation especially for the TEOS, MMF 10% and CC 0.6% treatments. It became evident that the efficacy of a treatment was depending on the WPG as well as on a homogenous distribution and penetration of the chemicals into the cell wall. However, for a deeper understanding of the protection mechanisms and influence factors, further studies are needed.

Table 5: Durability classification according to EN 350 (2016) after nine years of exposure

Treatment	Concentration	Approximate mean WPG/ retention	Decay rate [a^{-1}]	Durability class
MMF	10%	10%	1.33	M
	25%	25%	0.13	D
PF	25%	35%	0.62	M
TEOS	20%	25%	0.91	D
DMDHEU	0.8M		0.05	D
	1.3M		0.00	D
	2.3M		0.00	D
Acetylation (Accoya)		>20%	0.00	D
CC	0.6%	3.5 kg/m³	0.93	M
	2.5%	15 kg/m³	0.03	D
Scots pine sapwood			4.00	S
Radiata pine			4.00	S

CONCLUSIONS

Acetylation and modification with thermosetting resins at higher WPGs increased the durability against shipworms. Therefore, the modified wood has the potential to be used in sea water contact. Different protection mechanisms for the different modification systems are discussed in literature, but for a deeper understanding further studies are needed to investigate the influence of process and curing parameters as well as the distribution of chemicals. To assess the suitability of these treatments for building materials in marine environment, such as groins, jetties as well as sea bridges and poles, an upscaling to full size dimensions will be necessary in the future.

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