



**The Fifth European Conference
on Wood Modification
ECWM5**

September 20-21, 2010
Riga, Latvia

PROCEEDINGS

Edited by C.A.S. Hill, H. Militz and B. Andersons

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The Fifth European Conference on Wood Modification

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Preface

Modified wood is all around us - not only during these two days at the 5th European Conference on Wood Modification!

Facade elements, windows, doors, decking, garden furniture, parquet flooring, ship decks, even sauna benches: wherever wood has to meet high performance demands, nowadays it is likely you will find modified wood!

Things have progressed a long way since the 1990's, when a group of researchers from institutes, universities and industry assembled in the European Network on Wood Modification to exchange knowledge in this new field of research. Most of the experience those days was based on "normal" wood and preservative treated wood. New processes had to be developed, test methods adapted to a "new material", and markets to be convinced.

The first steps have been successfully negotiated. A handful of processes went down the stony road from laboratory scale to industrial level. The new material has now been commercialised and you can buy it in building supply stores. But with that, the need to exchange knowledge about all the challenges we encounter - from basic research to marketing aspects - does not end, but leads us into new territory.

New developments are under way. The community of researchers working and contributing to the still relatively new field of wood modification constantly grows. And with this, there is the need for a scientific forum to meet, present and talk.

This gathering of wood modification community will see 31 presentations and 29 posters being presented, some by recognised faces, some by newcomers to "our group".

Welcome to the 5th European Conference on Wood Modification!

Prof. Dr. Holger Miltz
Georg-August University, Göttingen

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Session One: Economics and Products

Material Evaluation and Product Performances of Beech Wood Modified with 1,3-dimethylol-4,5-dihydroxyethyleneurea (DMDHEU)

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Keywords: DMDHEU, Mechanical properties, Durability, Outside applications

ABSTRACT

Beech wood (*Fagus sylvatica*) is mainly used indoors because of low dimensional stability and weak resistance against basidiomycetes. Nevertheless utilization in new fields of application might be possible if these drawbacks could be improved. The objective of this study was to investigate Beech wood that was modified in an industrial process using three different DMDHEU concentrations. Together with industrial partners, different applications such as 1) plywood for two- or three dimensionally shaped beech wood, 2) picnic furniture 3) front doors 4) deckings, were investigated. The dimensional stability as well as the resistance against wood destroying fungi was improved. The latter was investigated in laboratory tests with brown- and white-rot fungi. A DMDHEU treatment results in an increase of hardness (BRINELL), compression strength and MOE, whereas bending strength did not change significantly. Shear and tensile strength were diminished, so was impact bending strength. DMDHEU treatment changes the crack performance of solid Beech wood. Internal cracks proceeded parallel to ray cells but become visible after planing only. Even after protracted process optimization, the crack performance was still critical. The evaluation of different applications showed DMDHEU treatment improving the outside performance of plywood for two- or three-dimensionally shaped Beech wood. The utilization of DMDHEU treated solid Beech wood is seen to be limited to applications where cracks are not of major importance.

INTRODUCTION

Beech wood (*Fagus sylvatica* L.) is a native resource, which is sustainably managed and long time available. Around 15% of the forest area in Germany is covered with Beech (BMVEL 2004). It is assumed, that different concepts within the German forestry will result in even higher availability of beech wood in the future (Hapla and Militz 2008). Beech is mainly used indoors because of low dimensional stability (Wagenführ and Schreiber 1974) and weak resistance against basidiomycetes (EN 350-2; 1994). New fields of application could be considered if these disadvantages could be improved. Within the last decades, a modification with N-methylol compounds has been investigated (Weaver *et al.* 1960; Nicholas and Williams 1987). Several publications show results from modification small solid wood samples in different tests. Especially the durability against wood destroying fungi as well as dimensional stability are increased after a modification (Videlov 1989, Militz 1993, Van der Zee *et al.* 1998, Van Acker *et al.* 1999). In the last years, publications also show, the feasibility of industrial modification of pine wood (Krause 2006, Schaffert 2006).

The objective of this study was to investigate the material properties of Beech wood modified in an industrial process using three different DMDHEU concentrations. Besides that, the suitability of the material for different applications was evaluated.

EXPERIMENTAL

Modification

Samples were made from Beech wood (*Fagus silvatica* L.) grown in the northern part of Germany. Before delivery, the material was kiln-dried. Predominantly the boards did not contain red heartwood, but a complete exclusion of this feature could not be obtained. The boards had a thickness of 43mm and a length of 2500mm. The width varied between 90-350mm. The boards were modified with various concentrations of 4,5-dihydroxy-1,3-dimethylolethyleneurea (DMDHEU), namely 0.8, 1.3 and 2.3M. Five percent of Magnesium chloride, relative to the weight of DMDHEU, was added as catalyst. Impregnation of the boards was carried out in an industrial process at the BASF SE Ludwigshafen by applying a vacuum of 60 mbar (30 min) and a subsequent pressure of 14 bar (2 h). A final vacuum step was used to remove excess solution. After the impregnation, the samples were cured in a hot steam dryer at a temperature > 135°C.

Material properties

Anti-Swell-Efficiency

The Anti-Swell-Efficiency (ASE) was determined according to Hill and Jones 1996. During this test, the samples were cyclically saturated with water (1h at 80mbar, storage in water for 24h) and subsequently dried to 0% moisture content (MC). After each water saturation- and drying step the dimensions were determined. A cycle was completed when the samples were anhydrous after a drying process over several days. The dimensions of the wood samples were 25x25x10mm³.

Durability

The durability of the material was tested adapted to CEN/TS 15083-1. All untreated and treated samples (30 samples of each combination) were exposed to the brown- and white rot fungi (Table 1) growing on malt agar in the laboratory under sterile conditions. The test duration was 16 weeks.

Table 1: Test fungi

	Fungus	
<i>Brown rot</i>	<i>Coniophora puteana</i> (<i>C. puteana</i>)	BAM Ebw 15
<i>Brown rot</i>	<i>Poria placenta</i> (<i>P. placenta</i>)	FPRL 280
<i>White rot</i>	<i>Trametes versicolor</i> (<i>T. versicolor</i>)	CTB 863A

Mechanical properties

Tests were conducted according to the standards shown in Table 2. For all test, 30 defect free samples of each combination were tested. Static tests were performed on universal test machines (ZWICK GmbH und Co. KG, Ulm Germany) with a 10kN or 100kN load cell. The results were evaluated with the software TESTEXPERT II (ZWICK GmbH und Co. KG, Ulm Germany). The impact bending strength was tested with an impact bending strength hammer HPSP 150. Prior to testing, all test specimens were conditioned at 20°C and 65% RH.

Table 2: Performed mechanical tests, test machines, samples sizes and used standards for all performed mechanical properties

	Test machine and maximum load	Sample size (rad x tang x long)	Standard Number and Year
Hardness, radial (BRINELL) [N/mm ²]	ZWICK 10kN	25x50x50 mm ³	EN 1534 (2000)
Tensile strength [N/mm ²]	ZWICK 100kN	20x20x300 mm ³ (Figure 1)	DIN 52 188 (1975)
Compression strength [N/mm ²]	ZWICK 100kN	20x20x30 mm ³	DIN 52 185 (1975)
Shear strength [N/mm ²]	ZWICK 10kN	25x25x25 mm ³	DIN 52 187 (1976)
Bending strength [N/mm ²]	ZWICK 10kN	20x20x360 mm ³	DIN 52 186 (1975)
MOE [N/mm ²]	ZWICK 10kN	20x20x360 mm ³	DIN 52 377 (1978)
Impact bending strength [kJ/m ²]		20x20x300 mm ³	DIN 52 189 (1975)

Tensile strength test samples had a total size of 20x20x300mm³. The thinner centre part had a size of 90x20x5mm³

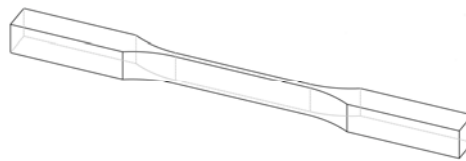


Figure 1: Tensile test specimens

RESULTS AND DISCUSSION

Material properties

Anti-Swell-Efficiency

An increase of dimensional stability by 25-35% (Figure 2) was found after a modification with DMDHEU.

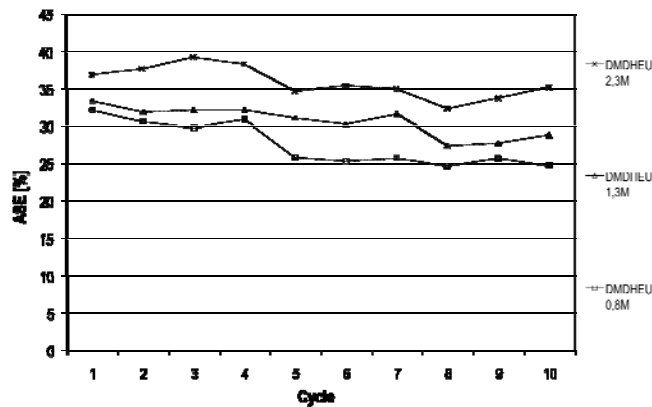


Figure 2: Mean ASE values depended on cycles and DMDHEU-treatment

Compared to literature, this increase of ASE is to be considered moderate only. Different authors described higher ASE values (Militz 1993; Yusuf *et al.* 1995; Van der

Zee *et al.* 1998; Krause 2006; Schaffert 2006). It is assumed that the different test designs account for different values.

Durability

The mass loss of treated samples compared to untreated samples indicates a significant increase of durability (Table 3).

Table 3: Mass loss [%] of DMDHEU treated samples and controls depending on test fungi

	Mass loss [%] (median and standard derivation)		
	Controls	DMDHEU 1,3M	DMDHEU 2,3M
<i>C. puteana</i>	36,52 (± 4,22)	8,50 (± 5,92)	0,59 (± 1,60)
<i>P. placenta</i>	21,09 (± 3,39)	0,44 (± 0,58)	0,67 (± 0,27)
<i>T. versicolor</i>	25,49 (± 5,22)	1,21 (± 3,55)	0,81 (± 0,84)

The following Table 4 shows the durability class according to CEN/TS 15083-1.

Table 4: Durability of treated and untreated Beech wood samples depended on test fungi

	Durability class according to CEN/TS 15083-1		
	Controls	DMDHEU 1,3M	DMDHEU 2,3M
<i>C. puteana</i>	5	2	1
<i>P. placenta</i>	4	1	1
<i>T. versicolor</i>	4	1	1

Mechanical properties

A DMDHEU treatment results in an increase of hardness (BRINELL), compression strength and MOE, however, bending strength did not change significantly. Shear and tensile strength were decreased as well as impact bending strength (Table 5).

Table 5: Mechanical properties of treated and untreated Beech wood

	Controls	DMDHEU 0,8M	DMDHEU 1,3M	DMDHEU 2,3M
Hardness (BRINELL) [N/mm ²]	39,94 (4,07)	64,75(12,85)	55,06 (15,22)	72,62 (26,20)
Tensile strength [N/mm ²]	147,60 (35,76)	102,48 (20,48)	101,15 (28,90)	90,19 (13,83)
Compression strength [N/mm ²]	61,32 (2,41)	86,46 (7,55)	90,35 (3,38)	101,23 (5,16)
Shear strength [N/mm ²]	13,96 (1,15)	8,02 (2,99)	5,67 (2,82)	5,82 (2,83)
Bending strength [N/mm ²]	104,97 (11,05)	99,77 (28,34)	84,71 (33,39)	94,83 (19,42)
MOE [N/mm ²]	13416,55 (1118,47)	14868,61 (1767,49)	16669,36 (2644,06)	14989,23 (1369,78)
Impact bending strength [kJ/m ²]	29,15 (6,40)	10,59 (3,12)	8,27 (2,89)	6,27 (1,16)

Applications

First products of DMDHEU treated solid Beech wood and Beech plywood were developed together with partners from the wood industry.

- Deckings and Picnic benches (FAHLENKAMP GmbH & Co., Bruchhausen Germany)
- Exterior door (VARIOTEC GmbH & Co. KG, Neumarkt Germany)
- Plywood for two- or three-dimensionally shaped beech wood chairs (BECKER KG, Brakel Germany)

Deckings and Picnic benches

The material for decking elements and picnic benches for outside application was produced in different processes at the University of Göttingen. The products were manufactured by the project partner FAHLENKAMP within a commercial process (Figure 3). Eight grooved boards (28x110x1400mm³) are screwed on 3 rails to produce decking elements. Some of the decking elements were arranged on the test field. The field was covered with gritting material to avoid direct ground contact (use class 3 application). In total, the size of the test field was around 30m². The remaining elements were used for decking in private use. Before outside application started, the material was treated to prevent blue stain (Pflegeöl 627, Sadolin). The benches were exposed on the premises of the University of Göttingen. The benches have direct ground contact (use class 4 application). The outside weathering trials for decking elements and picnic benches started in spring 2006.



Figure 3: Decking elements and picnic benches made from DMDHEU treated Beech wood

The conclusions of the material performance can be summarized as follows:

- The modification process was not optimal for Beech wood. Depending on the process in total, about 20-40% of the material had to be excluded because of cracks or other defects after modification.
- After more than 3 years of exposition, no decay is visible.
- After a short time of exposure (< 3 month) new cracks were detected.
- The amount of cracks and their size did not change significantly after the first 3 month.
- A commercial product against blue stain (Pflegeöl 627, Sadolin) was efficient. There are no signs of blue stain after more than 3 years of exposure.

Exterior door

Different exterior doors were produced by the project partner VARIOTEC. The material was modified at the University of Göttingen. Because the maximum length of the modified boards was 1400mm, the material was fingerjointed in order to obtain the required length. One-single leaf door was tested in a laboratory for building elements (Prüfzentrum für Bauelemente, Stephanskirchen, Germany) for air permeability, resistance to wind load, water tightness, operating forces and repeated opening and closing. The results were satisfying in all tests. A double door was installed in a technical building of the University of Göttingen in 2008. The properties of the door like tightness and dimensional stability are excellent. Decay has not been detected within the last two years. However, cracks comparable to those in the decking elements appeared after a short time (see below).

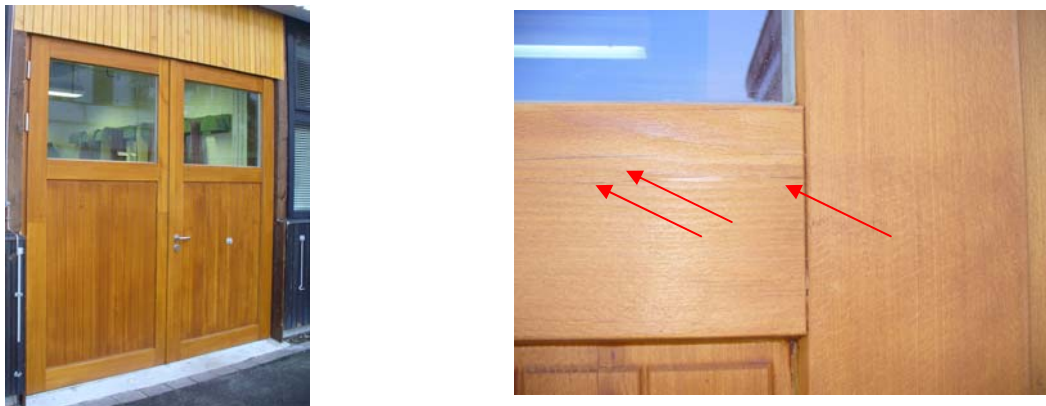


Figure 4: Exterior double door made from DMDHEU treated Beech wood

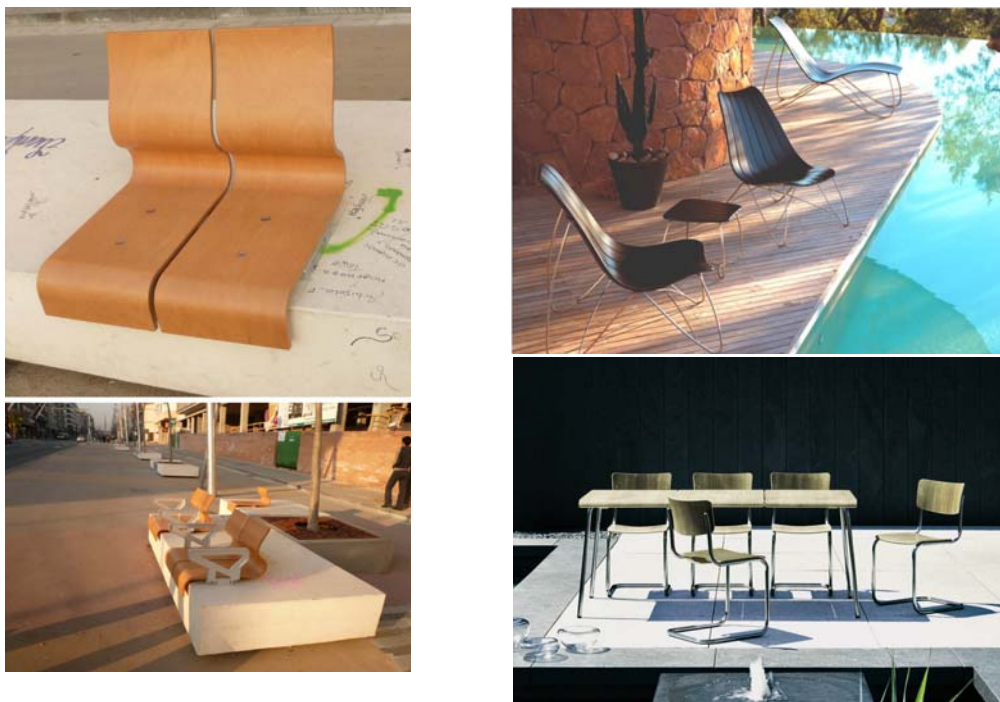


Figure 5: Plywood chairs made from DMDHEU treated veneers (BECKER KG, Brakel Germany)

Plywood for two- or three-dimensionally shaped beech wood chairs

All results showed that a modification with DMDHEU significantly improves durability and dimensional stability of Beech plywood. The project partner BECKER KG produced different prototype chairs and benches during the period of the project. The results indicated that the material is suitable for two- or three-dimensionally shaped Beech wood chairs. Nowadays, BECKER KG is able to produce DMDHEU modified chairs in serial production (Figure 5).

CONCLUSIONS

The material properties of DMDHEU modified Beech wood revealed that a treatment is possible and the material is suitable for outdoor applications. The dimensional stability as well as the durability (test adapted to CEN/TS 15083-1) is increased. As the results show, a concentration of 2,3M DMDHEU is necessary to reach durability class 1. Hardness and compression strength is increased relative to the concentration of DMDHEU. MOR and MOE did not change significantly. The decrease of impact bending strength and tensile strength indicated shortcoming of the material. The crack performance is poor; therefore the suitability of the material is seen to be limited to applications where cracks are not of major importance. The company BECKER KG sells DMDHEU treated beech veneer named BECKER BELMADUR. The outdoor performance, particularly dimensional stability as well as durability are increased and assure the products suitability for outdoor applications.

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Acetylated Wood in Structural Applications

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Keywords: Acetylation, Eurocode 5, mechanical properties, wood modification, timber engineering

ABSTRACT

Since the commercial introduction of acetylated wood on the market by Titan Wood in 2007, Accoya[®] wood has been applied in many different ways. In general, wood modification opens a whole new and broad range of innovative or renewed applications for timber. Timber may now also be used in structures previously made in steel, synthetic materials or concrete. An example is the heavy load-bearing traffic bridge constructed using Accoya[®] wood at Sneek in the Netherlands for which the whole process of design, fabrication, and project monitoring were commissioned by the principal to enable the bridge design and construction. All results are specific to this bridge and a second bridge of the same form is now in construction. Standardised testing is required to describe the performance of Accoya[®] in the wide range of structural application. This paper presents an overview of the properties of acetylated wood and discusses how this might be considered in the current regulations for structural applications.

INTRODUCTION

Use of wood in structural applications

Due to its properties (*e.g.* strength to weight ratio), its ease to process and its availability, wood has been used for structural applications throughout history. Wood is also a renewable material, which is, when used properly, completely in balance with the natural surroundings. However, since it is a product of nature, wood has a time limited life. At the end of its service life it goes back into its basic constituents of carbon dioxide and water through biological, thermal, aqueous, photochemical, chemical, and mechanical degradation processes. Most time limiting (durability) problems are associated with wood destroying fungi under high humidity conditions. Associated maintenance and decay risk raise, perceived or real represent the major barrier to increased use of timber in *e.g.* bridge design. Furthermore, due to water changes, moisture absorption and desorption, resulting in swelling and shrinkage, stresses develop, resulting in surface cracking (desorption) or internal cracking (adsorption).

Additionally, wood exposed to outdoor climate undergoes photochemical degradation caused by ultraviolet radiation.

The service life of untreated wood depends on the natural durability of the wood species. Many tropical hardwoods are known for their durability characteristics. However, a vast majority of the world's wood species do not possess inherent durability, dimensional stability and other valued characteristics. The world's supply of durable wood species suitable for long term performance in outdoor applications is becoming scarcer and there are detailed reports of second growth natural durable timbers failing prematurely (Araki *et al.* 2010). Furthermore, environmental regulations on the use of biocides (preservatives) to enhance the durability of wood are increasing. With special focus on the so called durable design, *e.g.* use appropriate covering for horizontal parts, part of the problems associated with natural durability of wood can be overcome. Further, by appropriate maintenance, wood can be fulfilling its purpose for a long time. However, nature is programmed to recycle and can have rapid effect when protective design systems fail.

Acetylated wood

An 'environmentally friendly' alternative is the chemical modification of wood which results in improved wood performance. By altering the wood matrix on a molecular level, the properties of wood species with low durability can be enhanced. Acetylation with uncatalyzed acetic anhydride is well known to increase the resistance of wood against wood decaying fungi as well as improving the dimensional stability under varying moisture conditions. The reaction of acetic anhydride with wood results in esterification of the accessible hydroxyl groups in the cell wall to acetyl groups with the formation of by-product acetic acid (see Figure 1).

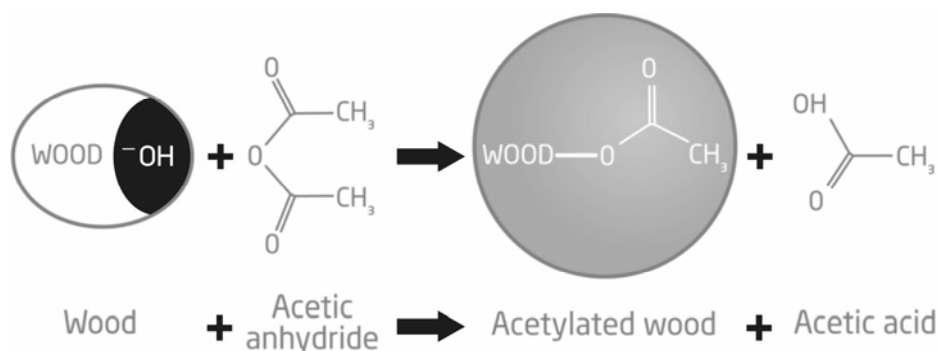


Figure 1: Schematic reaction of acetic anhydride with wood

A comprehensive background of acetylation and wood modification in general is given by Hill (2006), Homan and Jorissen (2004), Jones (2007) and Rowell (2006).

Titan Wood (www.titanwood.com) has introduced acetylated wood named Accoya[®] wood (www.accoya.com) on the market in 2007. Accoya[®] wood is based on the acetylation of radiata pine (*Pinus radiata* D. Don) and is mainly used for applications such as joinery, cladding, decking and (light) civil works in the Netherlands, UK and Germany (Alexander 2007, Bongers *et al.* 2009, Kattenbroek 2005).

Nowadays, the countries and market segments in which Accoya® wood are used is expanding. Furthermore, by acetylation of other wood species, new market segments can be addressed. Besides applications in which currently wood is used, acetylated wood, and in general modified wood treated differently, can open a whole new and broad range of innovative or renewed applications for timber where previously steel, synthetic materials or concrete was used. An example is the heavy load-bearing traffic bridge constructed using Accoya® wood at Sneek in the Netherlands (Tjeerdsma *et al.* 2007, Tjeerdsma and Bongers 2009, Jorissen and Lüning 2010).

USE OF ACETYLATED WOOD IN STRUCTURAL APPLICATIONS

The whole process of design, fabrication, and project monitoring of the heavy load-bearing traffic bridges in Sneek were guided by research institutes, working on behalf of the principal. Although many tests were performed, more standardised testing is required to fully describe Accoya® wood structural properties and enable its use in a wide range of applications. An overview of the current regulations and standards for structural applications and changed properties due to acetylation is presented below. The current certification schemes for modified wood are also described. Finally the service life and environmental impact of acetylated wood is discussed.

Regulations and standards

Wood used in structural applications needs to address the building codes and other regulations in the specific country. As part of harmonisation work in Europe within the Construction Products Directive (CPD) the required information of a building product is described for CE marking. The European Norm EN 1995, or "Eurocode 5: Design of timber structures" is a standardised European design code that establishes common rules across the European Union for structural design of timber buildings. The target of a designer is to ensure an adequately durable structure that fulfils the requirements of the building code and the principal / user. In order to do so many factors needs to be evaluated; for instance required performance criteria, expected environmental conditions, maintenance intervals and the composition, properties and performance of the used materials.

For wooden elements the resistance to biological organisms shall either have adequate natural durability for the particular hazard class or be given a preservative treatment. Furthermore, for structural application, "timber shall be strength graded in accordance with the rules ensuring that the properties of the timber are satisfactory for use and especially that the strength and stiffness properties are reliable". Either visual grading or machine graded timber according to EN 14081 series fulfils this criteria. The characteristic strength and stiffness values and densities should be determined according to EN 408 and graded according to EN 384. For glued laminated timber additional performance requirements are described in EN 386, finger joints shall comply with EN 387 and graded according to EN 1194. Finger jointed structural timber shall comply with EN 385.

Changed properties by acetylation

The polymeric structure of wood mainly consists of cellulose, hemicellulose and lignin. These components contribute in different ways and degrees to the mechanical properties

of wood (Winandy and Rowell 1984). Any chemical or thermal modification method that affects the chemistry of the wood cell wall polymers and/or their interactions must therefore affect the physical and mechanical properties of the wood (Rowell 1996). The affect will be different regarding different wood modification processes. A detailed study of the affect of thermal treatment on mechanical properties was made by Boonstra *et al.* (2007).

Due to acetylation, chemical changes of the wood cell wall polymers are evident; the moisture absorption behaviour of the cell wall is altered due to reactions of acetic anhydride with the hydroxyl groups. This results in a reduced Equilibrium Moisture Content. Furthermore, the density of the wood increases due the weight of the added acetyl groups. However, also the wood swells during acetylation resulting in fewer fibres per cross section than with the unmodified wood. The mechanical properties of acetylated wood have also been studied extensively, mostly on clear samples (Bongers and Beckers 2003, Dreher *et al.* 1964, Epmeier *et al.* 2007a, 2007b, Jorissen *et al.* 2005, Larsson and Simonson 1994, Norimoto *et al.* 1992, Rowell 1996, Rowell *et al.* 2009). Many researches concentrate on bending stiffness and strength. Tests to determine tensile strength, compression strength, shear strength, hardness, impact bending strength, creep and toughness have also been performed. However, based on the existing literature it is difficult to make hard conclusions on the exact number of the effects of acetylation on these mechanical properties due to variation in test results. This is most likely caused by the fact that the chemistry of the cell wall polymers and other characteristics vary (slightly) per wood species, within a wood species and even within a board. Furthermore, the type of applied acetylation process varies and even the affect on the properties can be different from one batch to another (Bongers and Beckers 2003). The variation of test results in larger elements, instead of small defect free sample, is increasing due to occurrence of defects in wood, such as knots, reaction wood, resin pockets, abnormal slope of grain and checks decrease the structural properties (Boonstra *et al.* 2007, Jorissen *et al.* 2005).

Besides mechanical properties, other properties, which are important for structural applications, are also changed by the acetylation process. Most obvious is the enhanced durability and dimensional stability of acetylated wood and its reduced response to climatic changes in relative humidity. However, other properties such as corrosion sensitivity of metals can also change. For glued laminated structures, bonding is important. Due to the physical and chemical changes of the wood due to acetylation not all commercially available adhesives are suitable and gluing processes need to be studied more in detail (Vick and Rowell 1990).

Design life expectation and environmental impact of acetylated wood

For any structural design, it is of importance to ensure an adequate design life. Although all materials are vulnerable for degradation, timber is considered to decay more quickly than steel or concrete in wet exterior applications. Inherently durable (or preserved) timbers can be used either partially or fully exposed to the weather. However, the only way to guarantee a life in excess of 35 to 40 years is to completely protect the structure from wetting (Lawrence 2008). A design life of 50 years for Ekki, 90 years for reinforced concrete and 50 years of (hot dip galvanized) steel was used in an environmental impact study of a typical pedestrian bridge (Van der Lugt *et al.* 2010). For Accoya[®] wood a design life of 80 years was used. Sustainable source Ekki has the

lowest environmental impact, followed by Accoya[®], concrete and steel. Unsustainable source Ekki has a high rating to account for the wastage of timber at forest sites where logs are harvested in this manner. Sustainably sourced timber bridges offer clear environmental benefit compared to non wood materials. Additionally Accoya[®] provides a long service life.

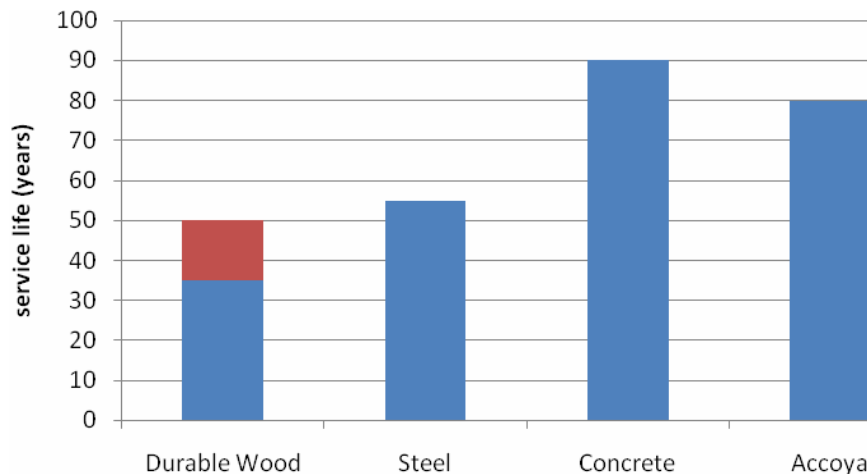


Figure 2: Design life of different building materials for timber bridges (sources Lawrence 2008 for durable wood and Van der Lugt 2010 for durable wood and others. Red section for durable wood expresses the differences in the two sources)

Certification and production control of modified wood

For market introduction, the building product has to at least comply with the building codes and regulations for the applicable market. In addition to these minimum requirements, certification may be demanded or strongly desired by the market. Certification can be divided into three categories: certification of the acetylation process, certification of the acetylated wood and certification of the final product. In the Netherlands, a National Assessment Directive was established to certify modification processes under the private label KOMO[®] (BRL 0605, Homan and Tjeerdsma 2005). Part of this certification is focussed on control of production consistency and repeatability of the process. The other part is related to the properties of the modified wood and is mostly concentrating on joinery applications. Based on these properties the modified wood can then be evaluated for its suitability in joinery in the Netherlands (SKH-Publicatie 97-04) and in Germany (VFF Merkblatt HO.06-4). In most countries, however, no schemes are available for evaluating modified wood.

Appropriate assessment for modified wood

For structural applications no specific evaluation schemes are available for modified wood. Widmann (2009) demonstrated the difficulties of introducing thermally modified beech (*Fagus sylvatica*) into the European strength class system EN 338. He concludes that the thermally modified beech should be regarded as a completely new material, rather than just a slight modification of a known wood species. Furthermore Widmann discusses the impact of the changed properties on various modification factors used in the Eurocode 5.

Regarding EN 1194 a serious problem arises. EN 1194 requires the basic properties bending strength, mean modulus of elasticity and density for determining other strength and stiffness properties. However, for evaluating the relationships given in EN 1194 untreated European (coniferous) wood species are used. It is not known whether these relationships hold for other species, like acetylated wood, as well.

Another discussion item forms the question if the testing methods currently used are still appropriate to test the behaviour of modified wood. When should machine strength grading be performed, after or prior to the acetylation? Most probably, the relationships used during machine test grading (machine settings) do not hold for modified wood and the settings must be developed completely.

CONCLUSION AND OUTLOOK

Despite the extensive scientific research noted on physical and mechanical properties of acetylated wood, more testing and model development is required to take the product forward through to an accepted structural approval. The impact of acetylation in literature varies by wood species, type of processes and between batch variations. Furthermore, the suitability of the current standards to evaluate the strength and stiffness properties of modified wood species as well as the design calculations may not be appropriate. Any approach taken will require support from appropriate production control including strength grading to ensure all building elements have the required properties.

In general many discussions exist regarding how to evaluate acetylated wood and in general modified wood for use in heavy structural applications. To harmonise effects in this area, involvement of the scientific community and legislation is critical. An option in Europe is the construction of an European Technical Approval (ETA), a harmonised standard or use of country specific approvals.

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Reinforcement of Thermally Modified Wood for Use in Highly Stressed Components of Musical Instruments

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Keywords: Carbon fibres reinforced plastics, dynamic fatigue test, experimental modal analysis, musical instruments, thermally modified wood

ABSTRACT

For the use of thermally modified wood for statically and dynamically highly stressed components of musical instruments, appropriate investigations were carried out at the TU Dresden. The comparative studies were performed on native and thermally modified maple (*Acer pseudoplatanus* L.) of unreinforced and reinforced cross sections. The cross sections were reinforced with carbon fibres reinforced epoxy resin in a single-stage process. Static and impact bending tests, dynamic bending fatigue tests and experimental modal analysis were carried out. Thus a characterization of mechanical and acoustical properties was possible. The results clearly show that thermal treatment improves the sound quality of wood. Additionally, the reinforcement with carbon fibre reinforced plastics will improve this. Static and dynamical properties of thermally modified wood increase by reinforcement, too.

INTRODUCTION

The use of wood in musical instruments requires a high quality of the material. The wood should have a high dimensional stability. Moreover, a high speed of sound is required and the wood should be free of growth stresses. Due to its reduced equilibrium moisture content and related high dimensional stability compared to local wood species, exotic wood is traditionally used in musical instruments. To achieve a complete reduction of growth stresses, the wood is dried over a period of many years. Furthermore, the stiffness of the material increases, thus the vibration damping decreases. This is known as natural wood aging. As a result of this time-consuming storage, high costs occur and the availability of suitable wood assortments is limited. Due to thermal modification of wood, i. a. the pore structure and the unsteady sorption behaviour are changed (Pfrieder *et al.* 2009, 2010). The degradation and transformation processes of the three main components of wood, especially hemicelluloses, during a thermal modification process, lead to an improved dimensional stability, increased speed of sound and a reduction in growth stresses. This could be described as an “artificial wood aging”. The improvement of the sound behaviour of thermally modified spruce (*Picea abies* (L.) Karst.) for sound boards of acoustic guitars was demonstrated by Wagenführ *et al.* (2006). However, its strength decreases due to thermal treatment. In particular, the high variation of the strength and stiffness values (Widmann 2009) is the main problem regarding the calculation and prediction of statically and dynamically stressed components. Therefore, thermally modified wood for construction components is not applied in civil engineering. One way to increase the strength and to reduce its variation values is the reinforcement of wooden cross sections with fibre reinforced plastics (Zauer *et al.* 2007). For civil engineering this procedure is too expensive, but it

is a very interesting field for musical instruments, especially for statically and dynamically highly stressed components, *e.g.* necks of guitars, bass guitars, and double basses. In one hand these components are responsible for resisting and transferring high forces. They are also significantly responsible for the sound of instruments. Studies of our own have shown that the wood species of the neck of electric bass guitars exerts a high influence on the acoustic properties of the complete instrument (Sproßmann 2008). Our main objectives in this work were to study the alteration of sound characteristics as well as static and dynamic properties due to thermally modification and reinforcement with carbon fibre reinforced plastics. The results should provide a basis for increase the use of thermally modified wood in musical instruments.

MATERIALS AND METHODS

Sample preparation

The investigations were carried out on native and thermally modified maple (*Acer pseudoplatanus* L.) of unreinforced and reinforced cross sections. The thermal modification was carried out on laboratory scale at a treatment temperature of 200°C and a treatment time of 4 h under nitrogen atmosphere on twin planks with dimensions of 200 x 55 x 400mm³ (rad x tang x long). The cross sections were cut from the twin planks and the dimensions of the specimens for experimental modal analysis, the static bending tests and dynamic bending fatigue tests were 20 x 20 x 360 mm³ and impact bending tests were 20 x 20 x 300 mm³ (rad x tang x long). For the samples with reinforcements, corresponding grooves were milled and the specimens were reinforced with carbon fibres reinforced epoxy resin in a single-stage process. This means, the fibre reinforced plastic was produced directly on the wood cross section and was simultaneously glued together with it. For this the pre-stressed carbon fibre rovings were inserted in the grooves. Then, the grooves were covered with holes-provided acrylic plates. Through the holes, the epoxy resin was injected with a disposable syringe. After curing of the resin, the acrylic plates were removed. The rate of reinforcement of the cross section was less than or equal to 3% and the fibre content of the carbon fibre reinforced plastics was 35%. The reinforcements were applied symmetrically on the tensile and pressure zones on the radial plane of samples. Thus, the test direction in all experiments was tangential. Conditioning of the specimens was done at 22°C and 65% relative humidity. In Figure 1, the preparation of the samples is pictured.

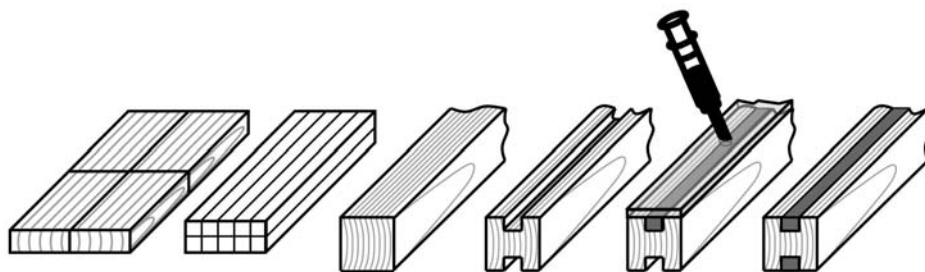


Figure 1: Manufacturing sequence for samples

Acoustic properties

The most frequently used parameter for characterizing acoustical properties of wood is the speed of sound c . For bar-shaped cross-sections the sound speed is defined in Eqn. 1.

$$c = \sqrt{\frac{E}{\rho}} \quad (1)$$

Where E is the dynamical modulus of elasticity and ρ is the density. Next to the speed of sound, Wegst (2006) also describes other acoustic parameters, e.g. the resonance quality R (Eqn. 2).

$$R = \frac{c}{\rho} = \sqrt{\frac{E}{\rho^3}} \quad (2)$$

Thus, the resonance quality can be calculated from the material parameters dynamic modulus of elasticity and density. Another characteristic parameter is the damping $\tan \delta$ (Bucur 2006), which is independent of E as well as ρ and describes in the audible range the viscoelastic behaviour of wood. This quantifies the damping of vibrations in wood due to internal friction (Wegst 2006) and is defined in Eqn. 3.

$$2\pi \tan \delta = 2\pi \frac{\Delta f}{f_r} = 2\pi Q^{-1} \quad (3)$$

Where Δf is the frequency width range of the resonance curve, f_r is the resonance frequency and Q^{-1} describes the quotient of both regarding the direction dependence in wood. The direction dependence in wood can be described as: $Q-1L \ll Q-1R < Q-1T$ (Bucur 2006). This means the damping in fibre direction is lowest. The investigations in acoustic properties were carried out by using the experimental modal analysis. This is a method of studying the dynamic properties of structures. Simplified, the transmission behaviour of a freely suspended specimen can be examined from an excited vibration. The analysis of the signal typically relies on Fourier analysis. As a result, the frequency and damping can be estimated from the corresponding mode shape. In experimental modal analysis, the investigated system is provided with a measuring grid, which exactly reproduces the structure and is sufficient for the number of the measured mode shape. For more accurate description, especially for the calculations of modal analysis, please refer to the relevant literature (Grimsel 1999, Wagenführ and Hardtke 2005). The test and evaluation method in our study is shown in Figure 2.

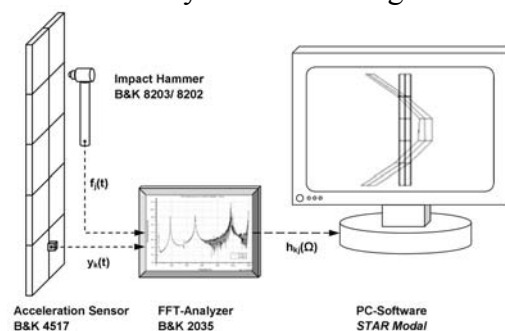


Figure 2: Test setup for experimental modal analysis

The vibration excitation was realized with an impact hammer and the impulse response was determined with an acceleration sensor. For the investigations only the first bending vibration mode was account as well as the corresponding natural frequencies and damping values are determined. Most of the samples for static and impact bending tests for dynamic bending fatigue tests were previously tested by experimental modal analysis. The sample size per series was 40 samples.

Mechanical properties

For the study of mechanical properties, static bending tests, impact bending tests and dynamic bending fatigue tests, each in three-point tests, were carried out. Each test comprised 25 specimens. The bending tests were executed according to DIN 52186 and the impact tests according to DIN 52189-1. For the latter test, a drop weight impact tester (Instron DYNATUP 8250) was used in place of a pendulum impact testing machine. This is justified because the kinetic energy of 50 J for pendulum impact testing machine according to DIN 51222 is too low to fracture the reinforced samples. The freefall velocity was selected to be 4 m s^{-1} when the drop weight hammer strikes the sample. With a fall height of 0.82 m and a drop weight of 12.1 kg, it was possible to realize a kinetic energy of the drop weight hammer of 70 J. The impact strength w was calculated from Eqn. 4.

$$w = \frac{1000 * W}{A} \quad (4)$$

Where W is the impact energy for fracturing the sample and A is the cross section of the sample. For the dynamic bending fatigue tests, the experiments were carried out at threshold fatigue area. The threshold value was set at the first bending deformation at a stress of 1000 N. The amplitude of oscillations around this threshold value was 2.5 mm and a frequency of 10 Hz was applied. The experiments were carried out up to a cycle number of one million. That means, one experiment lasted approximately 28 h.

RESULTS AND DISCUSSION

Sample parameters

The average values of the raw density and wood moisture content at 20°C/ 65% as well as the absolute wood mass lost due to thermal modification are given below (Table 1). As expected, the moisture equilibrium of thermally modified maple is significantly lower than the moisture equilibrium of native maple. However, the absolute mass lost is quite low. This is probably a result of the nitrogen atmosphere during thermal modification. Here, oxidation and hydrolysis processes are largely prevented.

Table 1: Compilation of the average raw densities, wood moisture contents and absolute mass lost

Sample	Raw density ^a [g cm ⁻³]	Wood moisture ^a [%]	Absolute mass lost ^b [%]
Unmodified maple	0.59	10.0	-
Modified maple	0.56	5.6	3.6

^aAt 20 °C/65 %, ^bdue to thermal modification

Acoustic properties

The results of the investigations of the acoustic properties in Figure 3 clearly show the improvement of sound characteristics due to thermal modification. A mean damping

value of 3.02 s^{-1} of modified maple compared to 4.16 s^{-1} of native maple, means a reduction of the damping by 27 %. This indicates a decreasing internal friction for vibrations in thermally modified wood. Due to the lower moisture content and the alteration of the pore structure (Pfriem *et al.* 2009, 2010), the sound propagation is improved (Wagenführ *et al.* 2006). The reinforcements with carbon fibre reinforced epoxy resin additionally reduce the damping of vibrations. An explanation is the better orientation of the carbon fibre in the test direction and the carbon fibre is built more homogeneous than the wood structure. Thus, the fibre reinforced plastic provides a lower resistance against the vibrations compared in wood (Zauer *et al.* 2007). The resonance quality values also show the excellent suitability of thermally modified wood for musical instruments. The sound characteristic will also be improved by reinforcements with carbon fibre reinforced plastics.

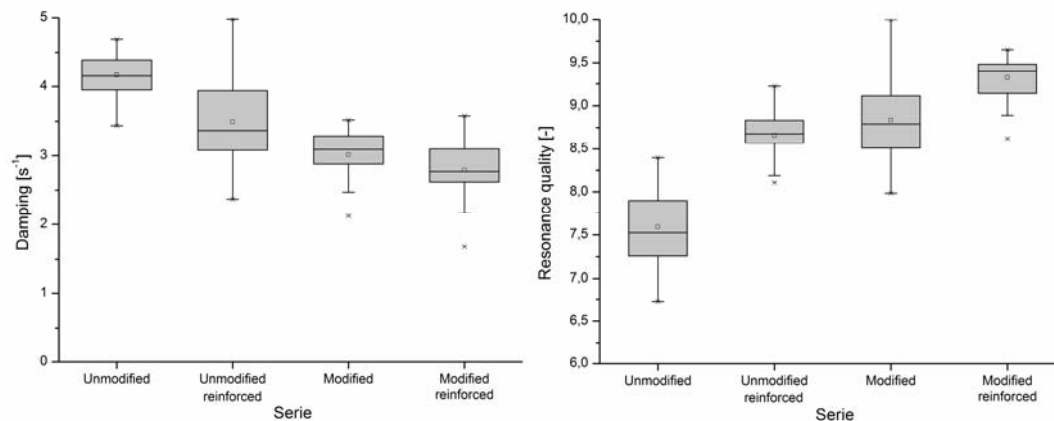


Figure 3: Damping values and resonance qualities measured by experimental modal analysis

Mechanical properties

Due to reinforcements with carbon fibre reinforced plastics, the bending strengths and stiffness's of native and thermally modified maple increase significantly (Figure 4). The reason for this is the very high stiffness of the carbon fibre reinforced plastics, which is located in the pressure and tensile zone of the wooden samples (Zauer *et al.* 2007). Compared to the stiffness of wood, its stiffness is about eight times higher. The strength of modified wood will be improved up to 28% and the stiffness of modified wood up to 41% because of the reinforcements. Demonstrative is the failure mechanism of the reinforced samples. The fracture begins with a plastic failure in the compression zone of the bending samples. As a result, the neutral axis moves to the tensile zone and in consequence of this, the wood fibre on the tensile side is highly stressed and fails. Significant is the reduction of the variations of the strengths and stiffness's due to the reinforcements. This means that by reinforcement the strengths and stiffness's will be homogenized. The stiffness of the modified samples is up to 7.5% higher than the values of the native samples (unreinforced and reinforced). The cause is the lower wood moisture content of thermally modified wood (Pfriem and Wagenführ 2008). Furthermore, the regeneration of lignin polysaccharide complexes and the increase in the number of cross-linkings within the lignin molecules lead to an increased stiffness (Wagenführ *et al.* 2006).

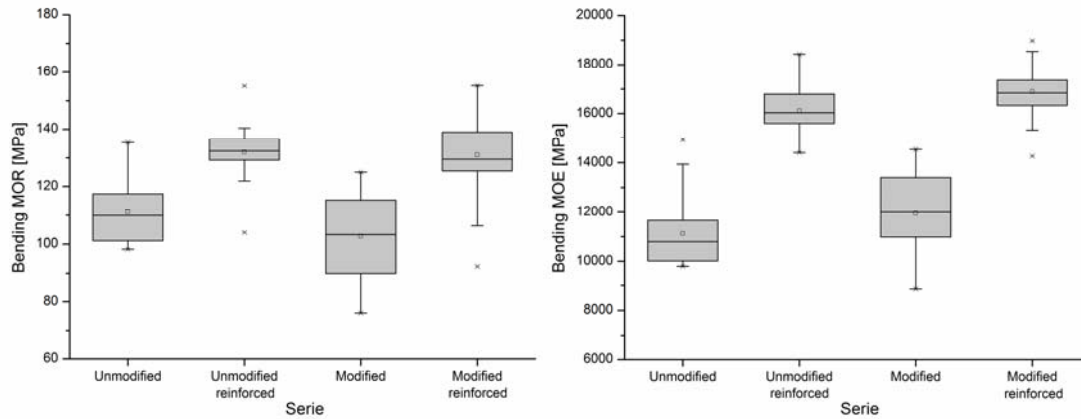


Figure 4: Bending MOR and MOE measured by static bending tests

The strength of unmodified maple is up to 7.6% higher than the strength of modified maple. The reason for this are probably the shortened molecular chains of cellulose as follow of the thermal treatment. The dynamical tests indicate also an improvement of short-time and long-term dynamical properties (Figure 5). The impact bending strength of thermally modified maple is up to 44% lower than the impact bending strength of native maple. Thus, thermal modification is the major effect on impact bending strength. The degradation of the hemicelluloses and the increase of the crystalline fraction of the cellulose, as well as the shortened molecular chains of cellulose during thermal treatment lead to an embrittlement of wood (Wagenführ *et al.* 2006). This can also be seen from the fracture morphology of samples. Due to reinforcements, the impact bending strength increases up to 2.4 times more for native maple and up to 3.8 times more for thermally modified maple. This means that the carbon fibre reinforced plastics compensate most of the kinetic energy.

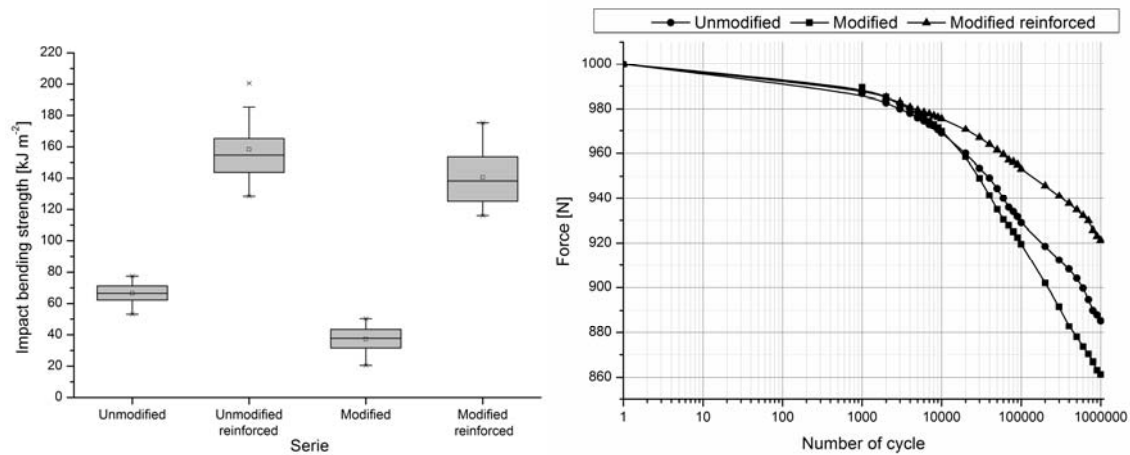


Figure 5: Impact bending strength measured by drop weight impact testing machine and decreasing forces due to dynamic bending fatigue stress

At this point it should be noted that results tested by a drop weight impact testing machine cannot be compared to those tested with a pendulum impact tester. Both methods are too different (Kollmann 1951). Our studies on unreinforced wood samples have shown that the impact bending strength determined by a drop weight impact tester is up to 30 % lower than the results determined by pendulum impact tester.

The Dynamic bending fatigue tests have not been completed yet. The recent results clearly show that reinforcements improve the fatigue stress behaviour (Figure 5). At a number of 20000 cycles, thermally modified wood shows a greater fatigue of material than native wood. Due to degradation of the hemicelluloses, the wood lost its elasticity. The “bonding agent” between cellulose and lignin is weakened and the wood fibres, especially libriform fibres and fibre-tracheids, glide better on each other.

CONCLUSIONS

The investigations clearly show the improvement of the sound characteristics of maple due to thermal modification. The damping values decrease and the sound qualities increase. As a result of the small reinforcements of unmodified and thermally modified maple with carbon fibre reinforced plastics, the sound of speed is also be improved. Moreover, the mechanical properties significantly increase and the variations of the strength and stiffness values decrease due to the reinforcements. Thus, a “homogenization effect” of mechanical properties occurs. The results clearly show the excellent suitability of thermally modified wood reinforced with carbon fibre reinforced epoxy resin for use in static and dynamical highly stressed components of musical instruments. Studies related to the sound characteristics of complete instruments, e.g. electric bass guitars with carbon fibre reinforced thermally modified wood in their neck, are currently carried out at TU Dresden.

ACKNOWLEDGEMENTS

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Modified Wood Entering New Markets – Findings in Wales and Portugal and How They May Affect Other Countries

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Keywords: Business development, heat treatment, marketing, modification

ABSTRACT

The importance of marketing the right product has gained importance in the wood modification sector. No longer can modified wood just depend on “being better than other materials”. There needs to be a greater awareness of client and customer perception, as well as financial considerations. Portugal and Wales represent small countries where the commercial application of wood modification may not bring the financial benefits to make it feasible. In the case of Portugal, this led to the exploration of supply from an established wood modification company (Plato International), using established links and experience to create links to local authorities, specifiers and planners. In Wales, the emphasis has been on the development of small scale heat treatment facilities capable of meeting local needs. This paper reviews both systems, attempting to outline their advantages and disadvantages and by looking at issues relating to marketing, promotion, proven track records and environmental considerations, show how they may help provide solutions for other countries where wood modification has yet to become established.

INTRODUCTION

Wood modification has become a recognised method for the delivery of enhanced timber, demonstrated through the success of this conference. Previously the success of a process or product could be solely linked to the properties afforded by the treatment (Jones *et al.* 2003). This is now only one part of a much more complex business plan. Many of the methods that have reached commercial exploitation have achieved so as a direct result of capital investment, either through the development of expensive processing, collaborative activities and/or international marketing. The ability to use in-house funding or raising funds through share schemes allowed processes such as Kurawood and Accoya the opportunity to expand globally, and more specifically into the South East Asia markets (TTJ 2007), projected in many material/commodity sectors as a key emerging/growing market. Typically, the majority of these internationally recognised processes are based around large and established market centres. One question arising from this is how can wood modification serve smaller markets and nations? Is there a preferable way to achieve wood modification without the need for considerable capital investment or by using local supplies in an innovative way? This

paper means to explore these options by looking at two different models, one chosen by Portugal and one chosen by Wales.

THE CURRENT WOOD MODIFICATION MARKET

Due to the economic downturn that begun towards the end of 2007, there has been little change in the wood modification market since the Fourth European Conference on Wood Modification (ECWM4). The major change has seen many of the companies operating in this area beginning to focus their activities on existing or perceived new markets. Previously, it could be argued that the benefits of the enhanced products were seen as sufficient entry points into a market. At ECWM4 (Jones *et al.* 2009), it was suggested that the success of modified wood lay in its ability to:

- 1) jump into an nice market where service is appreciated
- 2) be recognised as a superior product (as has been seen for computers with the “Intel inside” effect)
- 3) have the ability to enter new non-wood markets

Achieving these goals depend upon technical support of a product. The model adopted by Kebony (Westin and Lande 2004) typifies this, whereby the chain from sawmill to treatment plants to distributor/manufacturer to end user requires constant technical support. Among the key areas where this advice provides significant back-up to the marketing team are:

- Process know-how
- Access to patents
- Distribution of chemicals
- Documented properties
- Trademark concept
- Access to technology developments
- Marketing of the final product

Failure at any point throughout this technical support chain can lead to an ineffective market strategy.

Another example is the partnership between Reef/ TRC (the FSC concession holder in Cameroon) and Plato International. This helps ensure total control of the supply chain, the stock on the ground, the knowledge of a range of product-market combinations and a “push – pull” strategy towards architects. This combination allows for a successful and relatively quick market introduction of lesser and unknown tropical softwood species that have been modified using Plato Technology methodologies.

WOOD MODIFICATION IN PORTUGAL

Traditionally, Portugal represents a market where there has been significant interest in wood modification on a commercial level. There have, as with most other European countries, been activities at academic level, with interesting work undertaken by such groups as “Instituto Politecnico de Viseu” and “LNEC”, especially in terms of the modification of available Portuguese species. This work has led to a greater awareness and potential market options for furfurylated timbers.

However, the Portuguese market has a long standing trade link with Brazil, allowing relatively easy access to tropical hardwood species. This means the market is very conservative and extremely reactive to price fluctuations. This has been increased in the past two years due to the additional financial considerations resulting from the economic downturn. Additional doubt from specifiers relates to the suitability of certain timbers to the varied conditions across Portugal. One way of building a wood modification market in Portugal that has been identified has been for the wood treatment sector in Portugal seeking partnerships and association with well-established producers of modified wood.

Carmo, the leading manufacturer and supplier of treated wood in Portugal, has recognised the need for developing a partnership with a producer of modified wood. This has led to an association with Plato International of The Netherlands. One of the first steps in promoting the sale of modified wood in Portugal was to organise conferences aimed at local architects and overall specifiers. During these conferences, several presentations were given on the use of timber in general, highlighting the possibilities open when using modified wood, using cartoon representations of how timber properties have been altered (Figure 1). These meetings were organised in Lisbon and Oporto and were a tremendous success, generating a lot of interest in use of modified wood, and specifically, material from Plato International.



Figure 1: Cartoon depiction of the hydrophobicity of timber

In parallel to these conferences, specific training was given to Carmo's sales team, to better allow professional marketing of modified wood to current and potential new clients. To date, the Carmo sales' team has been active in presenting the product to a wide range of clients, from specifiers through to the final consumer. These actions are beginning to show results, with several orders now received, and more expected with the increasing acceptance of modified wood in Portugal.

The interest in modified wood in Portugal is not solely limited to Carmo. Another Portuguese firm, Jular, is pursuing a similar policy, through its association with Finn Forest, specifically for meeting the demands in decking and cladding.

The findings and experiences of companies to date to wood modification is that the material has a place in the Portuguese market, particularly for decking, pergolas and

cladding. This is already being demonstrated by the uptake of the material in several projects across the country. There is still the need for further education of Portuguese specifiers to the potential uses of modified wood, but as more projects are completed, some of these barriers may be reduced.

The modified wood market in Portugal is still in its infancy, but major inroads have been made over the past few years. Through further training, education, marketing and promotion of completed projects, it is anticipated that there will be further growth in the modified wood sector.

WOOD MODIFICATION IN WALES

There has been considerable interest in wood modification in Wales for several years, but implementation has been restricted due to financial considerations and supply of timber. Work at Bangor University explored most forms of wood modification, especially chemical modification (Hill and Jones 1996, Hill *et al.* 2003), whilst interest in thermal treatment was the focus of attention at Coed Cymru. Coed Cymru is an R&D centre in mid-Wales focussing on ways to improve opportunities for Welsh grown timbers. This interest led to the development of a 1 m³ heat treatment facility, operating under conditions not conflicting existing patents (*e.g.* ThermoWood).

Table 1 shows the main timber species of interest in Wales, along with the suitability of wood modification treatments. What Table 1 does not show is the dominance of one particular species, namely Sitka spruce (*Picea sitchensis*) as the main timber species produced by the Welsh forestry sector (currently accounting for approximately 70% of the total forestry output per year). The current Welsh forestry output is small compared to many other European and international countries (at approximately 0.8 million m³ per year), but the timber resulting plays a major role in some 1500 timber related companies across the country. Another key factor on market development in Wales is the size of woodlands in private ownership, with a high percentage of these within the size 0.5 to 10 hectares. In this way, the Welsh forestry sector could be said to have a similar forestry model to Denmark (Dugan 2004), where fragmentation has led to unwillingness to process wood into low value commodity sectors.

Table 1: Suitability of major Welsh timber species to wood modification techniques.

	Pine	Sitka spruce	Larch	Western hemlock	Beech	Birch
Acetylation	+	-	+	+	+	+
Fufrurylation	+	-	+	+	+	+
Oil treatment	+	-	+	+	+	+
Impregnation/ polymerisation	+	-	+	+	+	+
Heat treatment	+	+	+	+	+	+

The majority of the Welsh forestry output either enters the wood fuel/pulping market or high volume, lower-value produce. This means there is a continual low-return on timber production. Ideally, ways of adding value could bring a better financial return to the timber grower. This desire to add value, combined with a recognised desire by Welsh

companies to use locally sourced materials has generated a niche market for the development of heat treatment in Wales, especially using small scale facilities (Figure 2).

The result of the low temperature treatment undertaken was to achieve modified timbers where dramatic improvements in machining could result in higher quality products, particularly for the joinery sector. A significant advantage of the thermal processing undertaken has been the observation of adhesive fixing of knots in timbers such as European larch. This has enabled material of medium to high knot density to be used with confidence in higher value markets (such as external cladding).



Figure 2: Typical small scale heat treatment oven used in Wales

The heat treatment scheme in Wales has been shown to result in:

- Improved dimensional stability (lower likelihood of shrinkage and swelling).
- Better surface finishing (suitable for high end-value products), combined with a reduced risk of knot loosening.
- Inferred durability increase, but not to the levels of higher temperature thermal processes in operation across Europe
- Interesting colouration, typical of other heat treatment processes. However its application to uniformly bland coloured species, has been viewed as a way of adding value.
- Reduced hygroscopicity (less affinity to moisture), so less likelihood of movement in service.
- Increased opportunities for a range of Welsh timber species
- Reduced thermal conductivity values for treated timbers, providing an additional benefit in achieving low energy window systems.

These properties have been reported to joinery companies across Wales, and this has led to an expansion in interest in thermal processing, as shown by the number of facilities, typically with capacity around 4m³, now across Wales (Figure 3). Several joinery companies are now working together to manufacture window components incorporating thermally modified woods.

Due to the limited supply of high grade timber in Wales, the majority of work on thermal modification has been concerned with small dimension material, so maximising the potential benefits in creating high quality material for laminating.

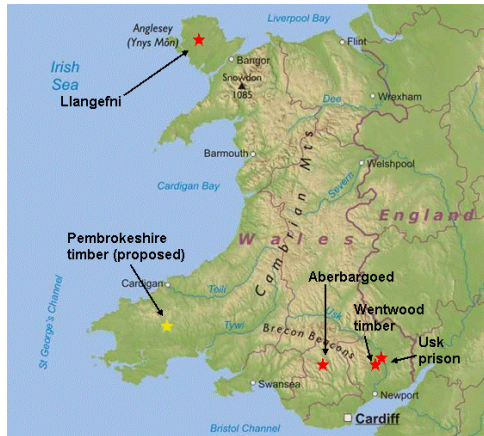


Figure 2: Heat treatment facilities across Wales

COMPARISON OF DEVELOPED MODELS

The market strategies defined herein effectively represent a mass market (adopted in Portugal) versus niche market (adopted in Wales). Table 2 (Hammett *et al.* 2006) gives a comparison between the two market formats:

Table 3: Comparison of market sizes and needs

Mass Market	Niche Market
Assume customers have similar needs, even in different regions	Based around customers having diverse, sometimes unique issues that need resolving
Have the ability to apply a common marketing approach	Market is often split into several concurrent themes
Products tend to be generic and can be promoted through a single activity	The need to develop and promote individual strategies.
Business plan based around: <ul style="list-style-type: none"> – Medium to long term profitability – Continual growth as recognition in a brand increases – Potentially a larger large of competing products – Demonstrating a definite financial benefit – Based on a proven track record. 	Business plan based around: <ul style="list-style-type: none"> – Short/medium term profitability – Rapid but potential limited growth – Limited number of competing products – Providing a competitive advantage – Often based around the loyalty of producers and occasionally end-users.
Customers with a recognised international scope of operation.	Customers with a small operating base dealing with local scope. Sometimes perceived as chauvinistic.

Delivering to the mass market can be viewed as simpler than dealing with niche markets as a standard approach will prove suitable to the multiple areas where it is being applied. The key issue with the niche market is that each case has to be reviewed, and a specific strategy developed.

A VISION OF WOOD MODIFICATION IN 5-10 YEARS

A snapshot analysis of wood modification in 2000 and 2005 shows the great advances made across the industry in those 5 years. These could be summarised as:

2000 – the inception of a modified wood market, greater understanding and collaboration initiated through the actions of the European Thematic Network for Wood Modification (under the 5th Framework Programme). A limited number of companies established, but limited market opportunities.

2005 – the presence of an established technical forum (the biannual European Conference on Wood Modification, as well as technical sessions at the annual International Conference on Wood Protection), a great number of companies active and marketing modified wood, increased numbers of examples of modified wood in use.

2010 - the expansion of market opportunities through adaptive marketing strategies (identifying a market gap and finding how modified wood can meet these needs), modified wood becoming the material of choice in selected market areas, greater innovative use of material.

Table 3 provides an estimate to the number of products where modified wood has become a commercially viable alternative to conventional materials. It can be seen from this Table that we have now reached a point where modified wood has become accepted as an option in delivering a range of products (such as cladding, decking, internal furnishing and musical instruments). The range of options for the use of modified wood is increasing, but the commercial acceptance of these products is still developing.

Table 3: Increase in commercial markets for modified wood

Year	Number of products	Description of products
2000	2	Cladding, internal timbers (<i>e.g.</i> saunas)
2005	5	As 2000, plus decking, canal linings, garden fencing
2010	10	As 2005, plus noise barriers, internal flooring, finger jointed/laminated combinations (<i>e.g.</i> for secondary structures and pergolas), windows, doors
2015		As 2010, plus cross laminated block boards, insulation applications (<i>e.g.</i> combination between different treated and untreated wood species/other materials), yacht decks, musical instruments, restoration applications, veneer manufacture.

It can be seen from Table 3 that market developments are increasing, demonstrating that modified wood is beginning to be perceived as the material of choice, no longer the material of luxury. The development of markets where modified wood is used in conjunction with other materials (*e.g.* steel, rubber, plastic, cork) will allow access to new market streams (including where soil contact or sea water contact is required). Wood is surely the most sustainable material on earth and modified wood excels in the characteristic combining it with added longevity and dimensional stability.

One of the key aspects for future development will deal with fire retardancy, allowing even greater market penetration. Providing solutions for emphasising the benefits from

using a sustainable material such as wood with the added benefits gained from wood modification will continue to offer specifiers with new opportunities.

CONCLUSIONS

Modified wood has come a long way since the early days of the Thematic Network for Wood Modification, and has still much to look forward to in terms of improving what it can offer. The development of new product ranges will allow for market entries in countries across Europe. This could be done through a collaborative approach with an established producer of modified wood (as has been done in Portugal), or through the development of individual processes meeting niche markets (as in Wales). The choice of model depends on the perceived medium to long term opportunities.

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Session Two: Chemical Modification

The Reaction Kinetics of Acetic Anhydride with Different Wood Species

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Keywords: Acetylation, kinetics, heartwood, sapwood, wood species

ABSTRACT

There are relatively few studies reported in the literature concerning the reaction kinetics of acetic anhydride with wood and those that do exist are usually concerned with studies on one wood species and sapwood only. As interest in the commercialisation of acetylation increases, there is a greater need to understand the influence of wood species and wood type upon acetylation. The purpose of this study was two-fold. Firstly, it was desired to compare the reaction rates of a range of softwood and hardwood species. The second purpose was to confirm whether the sapwood was more reactive than the heartwood. The results of these studies are reported and the results discussed.

INTRODUCTION

There have been relatively few papers reporting on investigations of the kinetics of the reaction of wood with carboxylic acid anhydride reagents. Hill and Jones (1996) reported on the reaction kinetics of propionic anhydride with Corsican pine (*Pinus nigra*) sapwood using pyridine as a swelling agent and catalyst. The reaction kinetics was interpreted in terms of a pseudo first order reaction and the activation energy (E_a) for the reaction was calculated using pseudo first order rate constants and from initial rates. The value obtained for the E_a was 23.8 kJ mol^{-1} (rate constants) and 31.3 kJ mol^{-1} (initial rates). Ramsden and Blake (1997) studied the reaction of acetic anhydride in xylene with four wood species (deal, Sitka spruce, southern yellow pine and larch) at three temperatures. Differences in the reactivity of the wood species were noted. Unfortunately, the absence of replication of wood samples used for the experiment and the use of only three reaction temperatures, makes the conclusions drawn from this study unreliable. The kinetics of the reaction of acetic anhydride with Corsican pine sapwood using pyridine as a catalyst and with pure anhydride reagent was reported by Hill *et al.* (1998). It was found that the reaction kinetics were diffusion limited and activation energies for the diffusion process were determined. For the non-catalysed reaction, the E_a was of the order of 34 kJ mol^{-1} , which was interpreted as being due to hydrogen bond breaking being the rate limiting step for diffusion into the cell wall. For the pyridine catalysed reaction, the diffusion E_a was about 20 kJ mol^{-1} . Activation energies obtained from initial rate data are considered to be more akin to chemical activation energies obtained under homogeneous reaction conditions. The activation energies obtained by the initial rates method for the uncatalysed reaction were 51 kJ mol^{-1} and for the pyridine catalysed reaction 42 kJ mol^{-1} . The uncatalysed reaction E_a

was found to be comparable with values reported for the acetylation of ethanol in solution. It was not possible to analyse the kinetics in terms of a pseudo first order reaction. Hill and Hillier (1998, 1999) and Hill (2003) reported on a comprehensive investigation of the reaction of different chain length anhydrides with Corsican pine sapwood under conditions of pyridine catalysis. It was found that as the reaction temperature was reduced and/or the chain length of the anhydride was increased the initial part of the reaction could be analysed in terms of pseudo first order kinetics, but became diffusion limited later on. The complex reaction-diffusion kinetics could be modelled very well by describing the movement of molecules on a square lattice according to percolation theory. The complex geometry of the lattice represents the interconnected nanopores in the cell wall whose geometry is controlled by the lignin/hemicelluloses matrix. The pyridine catalysed reaction of succinic anhydride (SA) and octenyl succinic anhydride (OSA) with Scots pine (*Pinus sylvestris*) was studied by Hill and Mallon (1998), with activation energies being obtained from the method of initial rates as 79.5 kJ mol^{-1} (SA) and 29.6 kJ mol^{-1} (OSA). Hill *et al.* (2000) studied the influence of different catalysts upon the rate of reaction of acetic anhydride with wood and noted that pre-impregnation of the wood resulted in an initially rapid rate of reaction, before the kinetics became diffusion limited. The activation energies were determined for the pyridine catalysed reaction of a series of linear chain anhydrides with Scots pine or Corsican pine sapwood by Hill and Papadopoulos (2002). Activation energies calculated from rate constant or initial rate data were found to decrease as the molecular weight of the anhydride increased, an observation also supported by the findings of Özmen and Çetin (2003). Hill and Papadopoulos (2002) attributed the reduction in the rate constant or initial rate E_a as molecular weight of anhydride increased, to the constraint applied on molecular motion within the narrow nanopores within the cell wall. Meanwhile, Hill and Papadopoulos (2002) did not find any relationship between molecular weight of anhydride and diffusion activation energies. Minato and Ogura (2003) studied the reaction kinetics of Sitka spruce (*Picea sitchensis*) (wood meal and wood block) with acetic anhydride in the absence of solvent, with xylene and with pyridine catalyst. They curve-fitted the kinetic data using nonlinear regression in order to obtain the rate constant for the reaction, using the assumption that pseudo first order kinetics would be observed throughout the reaction. Much higher activation energies were obtained than reported by Hill *et al.* (1998). However, the study of Minato and Ogura (2003) can be criticised on a number of grounds: (a) the reaction kinetics is not pseudo first order, (b) the use of non-linear curve fitting requires highly accurate data to give reliable results, (c) only a few temperatures were used for the Arrhenius plots. The rate equation used by Minato and Ogura (2003) was modified by Minato (2004) to account for the influence of diffusion on the kinetics. However, the scatter in both the kinetics data and the Arrhenius plots gives reason to treat the reported activation energies with great caution. The modified rate equation was also used by Minato and Ito (2004) to study the relative influence of wood swelling and chemical catalysis upon the acetylation of Sitka spruce. The influence of delignification upon the rate of reaction of wood with acetic anhydride has been studied by Haque and Hill (1998, 2000) and Minato *et al.* (2007). Haque and Hill (1998, 2000) found that complete delignification resulted in an increase in the rate of reaction, whereas Minato *et al.* (2007) found an increase in reaction rate initially and then a decrease as the extent of delignification was increased. There have been relatively few studies where the influence of wood type upon the rate of reaction has been reported. Hon and Bangi (1996) found that reactivity of oriented strand board flakes to acetylation increased in proportion to juvenile wood content, although there was no difference found when

moving from the core to the outer part of the tree. Rowell and Plackett (1988) found no difference in the reactivity of heartwood and sapwood when acetylating flakes of *Pinus radiata*. However, differences in the reactivity of heartwood and sapwood have been reported for larger wood specimens (Beckers and Militz 1994). Differences in reactivity between different wood species have been reported by Rowell *et al.* (1986) and Beckers and Militz (1994). The purpose of the present study was to examine the influence of wood species and heartwood and sapwood upon the rate of reaction and reaction kinetics of acetic anhydride with wood.

EXPERIMENTAL

Wood blocks (Japanese larch: *Larix kaempferi* (Lamb.), Korean pine: *Pinus koraiensis* Siebold et Zucc., Korean oak: *Quercus aliena* Blume, European beech: *Fagus sylvatica* L.) of dimension 20 mm x 20 mm x 5 mm (radial x tangential x longitudinal) were used for this study. Heartwood and sapwood were studied in all but the case of European beech (sapwood only). The wood samples were Soxhlet extracted in a mixture of toluene/acetone/methanol (4:1:1 by volume) for 8 h, left in a fume cupboard for 24 h to allow the majority of the solvent to evaporate and then dried in an oven set at 105°C for 24 h. The blocks were removed in an oven and placed in a desiccator over silica gel to cool to ambient temperature. The oven-dry weight and dimensions were then determined. Prior to reaction, the wood samples were impregnated with acetic anhydride at ambient temperature for one hour. A reaction vessel containing acetic anhydride situated in an oil bath was maintained at 100°C for the duration of the experiment. The acetic anhydride saturated samples were added to the reaction vessel in batches of 12 at specific intervals to give reaction times of (15, 30, 45, 60, 75, 105, 165, 285, 405 and 1285 minutes). At the end of the reaction, the hot reagent was carefully decanted off and the still hot blocks dropped into ice-cold acetone to quench the reaction. After one hour in the acetone, the samples were transferred to the Soxhlet apparatus for extraction using the standard solvent system, then oven-dried as described previously before weight and dimensions were recorded as described previously.

RESULTS AND DISCUSSION

Comparisons in the reactivity of sapwood and heartwood for Japanese larch, Korean pine and Korean oak are shown in Figure 1. The graphs on the left hand side are standard reaction curves plotted as WPG against time in minutes, whereas the graphs on the right are diffusion plots showing the number of OH groups substituted against square root time. The kinetics are diffusion limited during the initial stages of the reaction and as the number of available reactive sites becomes limited during the later stages of the reaction, there is a change in the kinetic behaviour. There is little difference in reactivity between heartwood and sapwood for the two softwood species, but there is a large difference for Korean oak. However, when the kinetics is plotted in terms of diffusion, some interesting details emerge. For the two softwood species, these subtle differences are probably not statistically significant, but for Korean oak, the large difference in reactivity is not due to a difference in the rate of diffusion, since the gradient of the two lines is the same. Rather, the difference is related to an induction period in the reaction with heartwood (there is also an induction period with the sapwood, but to a lesser extent). This is thought to be due to the removal of extractive substances from the oak by the hot acetic anhydride. Prior removal of extractives by solvents may not in the case of oak remove all of the extractable material. With the two softwood species, the lines

on the diffusion plots do not project through the origin because the cell wall is previously impregnated with acetic anhydride. It is only when this cell wall located reagent is used up that the reaction kinetics move over to being diffusion limited.

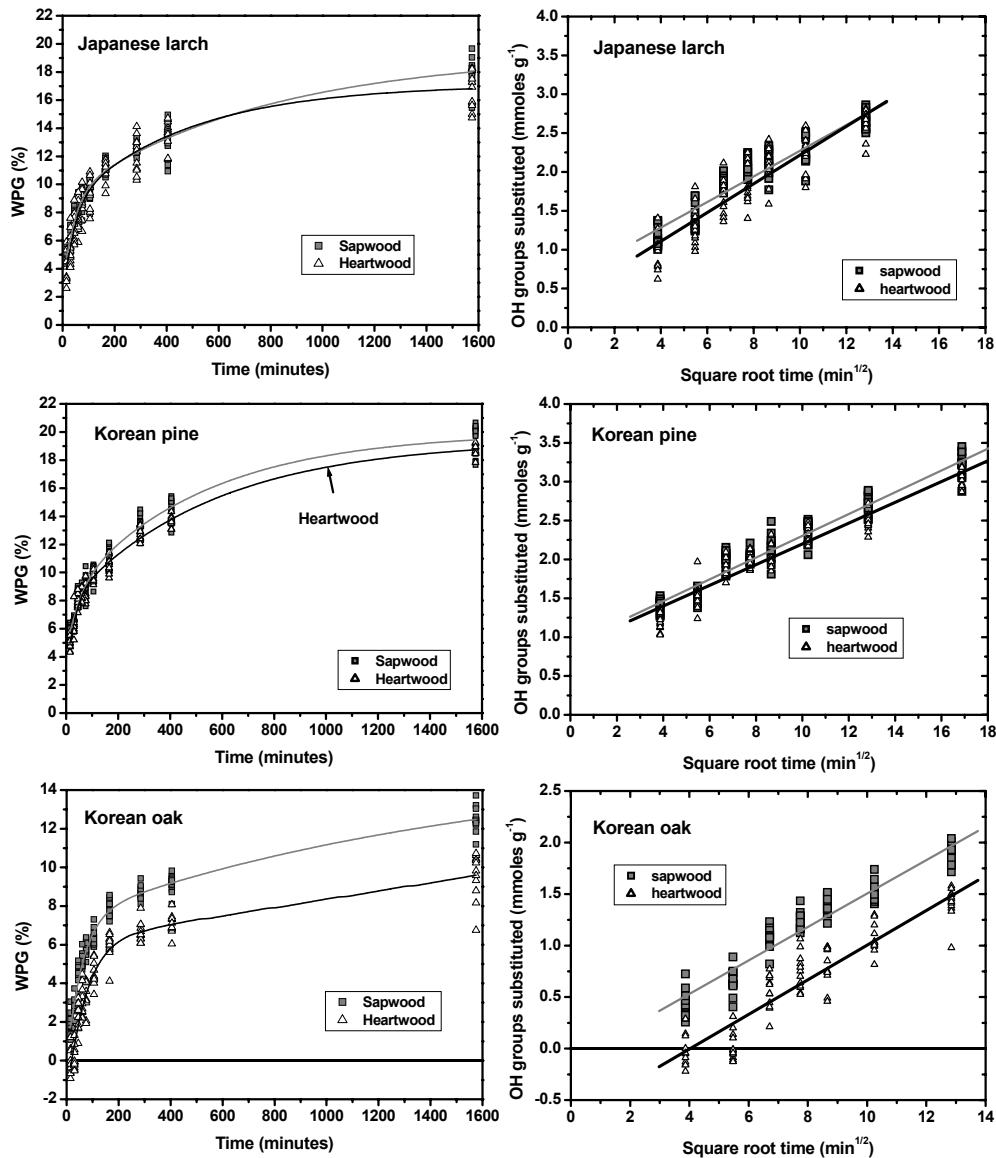


Figure 1: Comparison of kinetic curves for Korean pine, Japanese larch and Korean oak showing differences in sapwood and heartwood reactivity

Differences in the reactivity of the wood species are shown in Figure 2. For both heartwood and sapwood, the order of reactivity is Korean pine>Japanese larch>European beech>Korean oak. However, during the initial stages of reaction (up to 200 minutes) when the reaction kinetics is analysed in terms of diffusion (Fig. 2, rhs) there is little difference in the rate of reaction between the different wood species, although Japanese larch is slightly more reactive than the other species studied. This was found both for sapwood and heartwood reactivity. The possible influence on wood density was examined by plotting the WPG obtained at 1575 minutes against wood density of the samples (Figure 3). This shows that as wood density increases, the

reactivity of the wood decreases. No such relationship was observed for the diffusion limited regime of the kinetic profile.

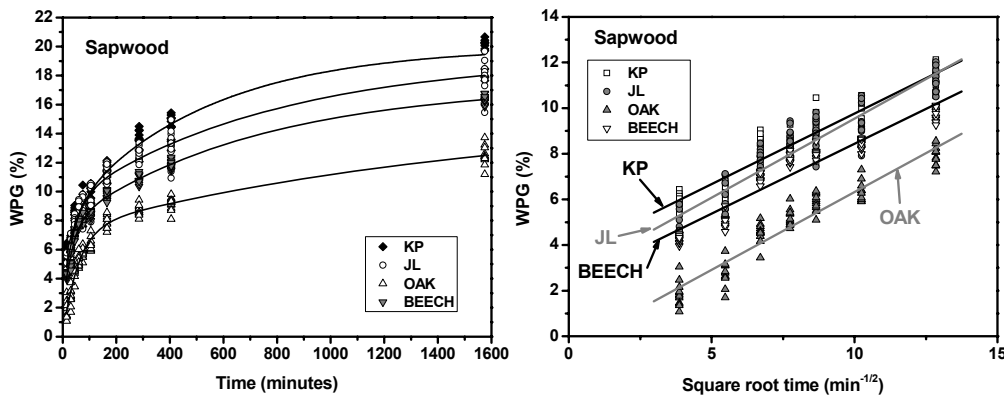


Figure 2: Differences in reactivity between wood species, showing reaction profiles (lhs) and diffusion kinetics (rhs)

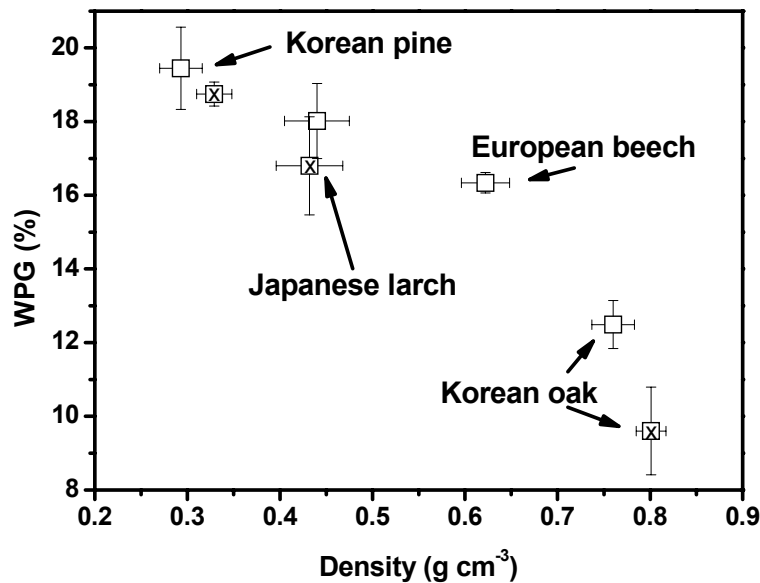


Figure 3: Relationship between wood reactivity (defined as WPG at 1575 minutes) and wood density for heartwood and sapwood, boxes marked with an 'x' are heartwood

The effect of density upon reactivity was further investigated by reacting Corsican pine blocks in pure acetic anhydride at 100°C for two time intervals to give two target WPG's. The results of this study are shown in Figure 4 and the statistical data from the linear regression analysis of the data is given in Table 1 below. Both of the linear regressions represent negative correlations between WPG and density. Although the correlation is weak, as shown by the low R values, both fits are nonetheless very significant, with very low p values. This observation supports the finding that an increase in wood density leads to a reduction in reactivity with acetic anhydride.

Table 1: Statistical data for the linear fits in Figure 4

Fit	Gradient (WPG g ⁻¹ cm ³)	R	p
a	-14.65	-0.394	<0.0001
b	-13.85	-0.293	4.43 x 10 ⁻⁴

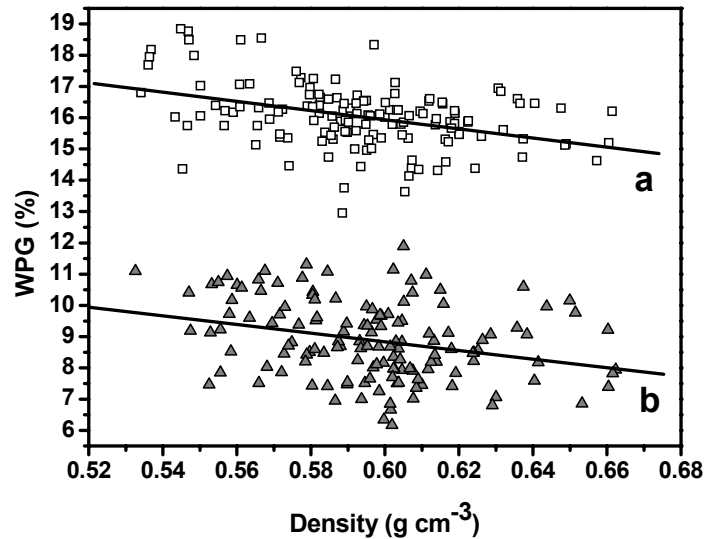


Figure 4: Graph showing relationship between wood density and reactivity to acetic anhydride for Corsican pine sapwood

CONCLUSIONS

This work has shown that there is no substantial difference in the reactivity between the heartwood and sapwood of Korean Pine and Japanese larch. Although there is a difference in the reactivity between the heartwood and sapwood of Korean oak, this appears to be related to the removal of extractives by the hot acetic anhydride rather than to any inherent difference in reactivity. There are differences in the reactivity between various wood species, although this does not appear to be the case in the diffusion dominated part of the kinetic profile. The differences in reactivity between species appear to be related to differences in wood density and this has been confirmed in a separate experiment with Corsican pine sapwood.

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Influence of Acetylation, Moisture, and Heat Flux on Reaction to Fire in Cone Calorimeter Tests of Pine (*Pinus sylvestris* L.) Wood

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Keywords: Wood, acetylation, cone calorimeter, reaction to fire, moisture content, heat-flux

ABSTRACT

This work is a follow-up of previous research on the fire performance of acetylated wood as a construction material. It was found that wood acetylation prolongs the time to ignition and decreases smoke production, when acetylated wood is conditioned at 296 K and 50% relative humidity according to EN 13238:2002 is burned. Absorbed water in wood could be considered as a counter-fire agent. Oven dried acetylated and reference wood specimens were used in cone calorimeter tests to get a better assessment of the wood acetylation effect on reaction to fire, because practically it is impossible to equate initial water content in acetylated and reference wood due to different EMC. Reaction to fire tests was performed on a cone calorimeter according to ISO 5660-1:2002 with horizontal specimen positioning. Heat fluxes of 30 kW m⁻², 50 kW m⁻² and 75 kW m⁻² were used to evaluate heat flux effects. Pine (*Pinus sylvestris* L.) wood specimens 100 mm x 100 mm x 19 mm were exposed to an intensive acetylation process to obtain acetylated wood with a maximum acetylation degree and a more even acetyl group distribution. Mass gain by the acetylation of pine wood was 29 – 31 %. The impact of wood acetylation, species of wood, moisture content, and external heat flux was evaluated as the ratio of difference between values of indicators of tested and reference samples for: time to ignition, time to flame-out, heat release, mass loss rate, smoke production, carbon monoxide, dioxide yields *etc.* Effect of species was evaluated by comparison of pine wood test results with hardwood species at 50 kW m⁻² heat flux. Practical recommendations for acetylated wood fire safety are proposed.

INTRODUCTION

Wood is one of the oldest materials used by man. Wood has been used for a wide range of applications because of its availability, low cost, ease of processing and its mechanical properties; but as a lignocellulosic material, it is subjected to matter circulation in the biosphere and it is colonised and decayed by bacteria, fungi, and insects at the end phase. Biological deterioration can be diminished by a drastic decrease of water content in wood below the fibre saturation point. Drying increases wood mechanical durability but in same time causes significant problems for structural timber components in buildings due to the wood-moisture-interaction in changing humidity that causes dimensional alteration. Wood properties result from the chemistry of cell wall components and can be consequently changed by modifying the basic wood-water interacting hydroxyl group. “Wood modification is a means of altering the material to

overcome or ameliorate one or more of its disadvantages” according to Hill (2006). Chemical modification of wood cell wall substance had increasing interest world wide in last decades (Rowell 1983, Kumar 1994, Morozovs *et al.* 2003) Wood acylation with acetic anhydride is the most well-known modification process. Hydroxyl group acetylation improves wood dimensional stability and decay resistance (Kumar 1994, Hill 2006) and reduced fibre saturation point of wood (Hill 2008). In the process of selecting new or alternative materials for applications in the built environment, it is necessary to consider the fire performance of the material. Any changes in wood chemistry would change wood reaction to fire. It is required that the materials selected for use must be evaluated in flammability tests to estimate their role in the development and survivability of fires (Panagiotou and Quintiere 2004). Anyone could suppose that acetyl groups could be eliminated from acetylated wood as acetic acid in conditions of pyrolysis. Acetic acid is a flammable volatile substance that would be expected to increase the flammability of acetylated wood. However, acetylation increases wood density that will cause a decrease in its reaction to fire (White 2002, Njankouo *et al.* 2005). The objective of this investigation is to extend previous investigations in the fire performance of acetylated wood (Morozovs *et al.* 2007, Morozovs and Bukšāns 2009 a, b) estimating the influence of wood chemical modification with acetic anhydride as well as the moisture content in wood, external heat flux and species of wood on the wood reaction to fire using the cone calorimeter tests.

EXPERIMENTAL

Materials

Defect free, straight grained pine (*Pinus sylvestris* L.) aspen (*Populus tremula* L.), birch (*Betula pendula* Roth.), grey alder (*Alnus incana* (L.) Moench.), oak (*Quercus robur* L.) heart woods were sawn and planed to give specimens corresponding fibre, tangential and radial direction 100 mm x 100 mm x 20 mm at 293°C and 65% RH. The wood specimens were dried at 373±2 K till constant mass. The oven-dried wood specimens were placed in a reactor with 1.5 mm wood sticks as separators between specimens and vacuumed at 2 mbar residual pressure for 12 h, then acetic anhydride was introduced into the reactor under vacuum and the wood was impregnated in immersed conditions for 24 h, then excess acetic anhydride was poured off and the reactor was heated up to 393 K and kept at such temperature for 12 h to accomplish the acetylation reaction. During acetylation, any exuded mixture of acetic acid and acetic anhydride was periodically poured off to keep the wood specimens dry. Thereafter, wood specimens were vacuumed to distil off acetic acid and un-reacted acetic anhydride. The reactor was cooled and then wood specimens were dried in an oven at 376±2 K till constant mass and without any smell of acetic acid. Acetylated wood specimens were arranged by mass percentage gain (MPG) and a series of 3 specimens with the highest MPG and low dispersion were selected for cone calorimeter tests. Reference wood samples were kept in an oven at 376±2 K for the same period as sum of acetylation and drying times of acetylated samples to compensate for the impact of long time exposure at elevated temperature.

Cone calorimeter tests

Cone calorimeter tests were realized on the Dual Cone ISO 5660 (Fire Testing Technologies Ltd) till flame extinguishment in accordance with ISO 5660-1:2002, to reduce the influence of smoldering combustion on test results. Wood specimens were

tested in a horizontal orientation and covered with aluminium foil except for the exposed surface. Acetylated and reference Scots pine wood specimens were tested oven dried or conditioned according to EN 13238:2002 with heat flux of cone heater set at (30, 50 or 75) kW m^{-2} to evaluate acetylation, moisture in wood and heat flux value effects. Pine aspen, birch, grey alder, and oak specimens were tested conditioned according EN 13238:2002 and the heat flux of cone heater was set at 50 kW m^{-2} to evaluate wood species effect.

Thermal diffusivity tests

Specimens with 3 replicates (100 mm x 100 mm x 100 mm) were cut from spruce (*Picea abies* L.) wood single glulam beam glued with thermo reactive glue. Seven K-type thermocouples were placed in each specimen from the lateral side in 2 mm diameter holes drilled parallel to the exposed surface to the centre of sample exposed surface with 5 mm, 15 mm, 25 mm, 35 mm, 45 mm 55 mm and 65 mm distance from initial surface before the test. Conditioned according EN 13238:2002 each specimen was tested with exposed surface in the vertical configuration without piloted ignition. Wood specimen was installed in sample holder made from calcium silicate board (Fig. 1).



Figure 1: The wood specimen with thermocouples fitting in sample holder with removed thermo-isolation

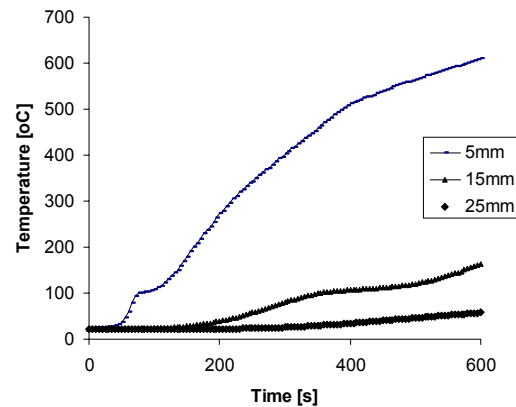


Figure 2: Temperature alteration curves in 5 mm, 15 mm and 25 mm depths from exposed surface

Lateral and back sides of the specimen were isolated with mineral wool and a calcium silicate container. The cone calorimeter heater was set to a heat flux of 50 kW m^{-2} . The average moisture content of the specimens conditioned at 296 K and 50% RH till constant mass was about 11%. Temperature data from seven thermocouples were electronically recorded at 5 second intervals with a data logger and saved. Temperature alteration curves (Fig.2) in different depth from exposed surface inside wood were constructed from saved data.

RESULTS AND DISCUSSION

Hydroxyl group substitution with oxyacetyl groups by wood acetylation improves wood's durability (Rowell 1983, Kumar 1994, Morozovs *et al.* 2003, Hill 2006). Nowadays acetylated wood has become commercial product (Tjeerdsma and Bongers 2009). Large scale application of such products raises issues regarding the evaluation of potential hazards and risks of exploitation of new product such as acetylated wood because its chemical composition is changed to a considerable extend in comparison

with un-modified wood that causes changes in its chemical and physical properties. The wood substance hydroxyl group's hydrogen atom substitution with acetyl group alters its chemical nature. The oxyacetyl group could be more easily eliminated in comparison with hydroxyl group due to delocalisation of unpaired electron between both oxygen and carbonyl atom of oxy-acetyl group (Figure 3) that could not be possible in case of hydroxyl group elimination.

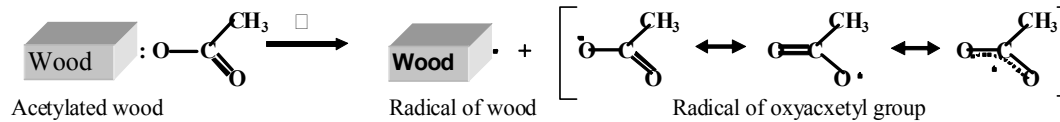


Figure 3: Mesomeric structures of oxyacetyl group

Easier elimination of the functional group would increase amount of gasiform product formation and as consequence increased product flammability. Acetylation increases wood mass and carbon content in it that enlarges its heating capacity and would produce higher heat release, when the modified wood is burned.

Impact of wood moisture content and acetylation interaction on fire performance

Water in wood can act as a fire extinguisher due to large amount of energy need to evaporate water, which prevents temperature increase above water boiling temperature (373 K) that delays wood temperature increase so necessary for wood pyrolysis (Buksans and Morozovs 2007) (Figure 2). The first three thermocouples showed the presence of a plateau in temperature curves at approximately 373 K. This plateau becomes wider for the deeper thermocouple. The plateau width depends from temperature gradient and moisture content in the given point. The heat flux through plane in 5 mm depth in wood is higher than in 15 mm depth from the exposed to heat flux surface due to heat transfer resistance of wood. The low thermal diffusivity of wood is one of reasons for char layer formation. Chemical changes by acetylation in wood would influence its thermal diffusivity. Acetylated wood has reduced equilibrium moisture content in comparison with untreated wood (Hill 2006, Hill 2008). To evaluate the impact of acetylation on wood fire performance, it is necessary to compare wood samples with equivalent water content. It is practically impossible to obtain acetylated and reference wood specimens with equal moisture content. Additionally, at increased temperature water could intensify acetyl group hydrolysis in acetylated wood that would cause misinterpretation of acetylated wood reaction to fire. To take this into account oven dried wood was used to evaluate wood reaction to fire alteration by acetylation. Oven dried un-modified wood specimens were used as references. During acetylation wood is exposed to increased temperature at 396 K and drying at 376 K for long time therefore reference wood was exposed at 373 ± 2 K for the same duration. Acetylation increased by 32% the time to ignition of modified wood under 50 kW m^{-2} heat flux, as well as intensified wood burning by 8% in comparison with reference wood when oven dried wood specimens were tested (Figure 4). If wood contains absorbed water, then conditioned according EN 13238:2002 at 23 °C and 50% RH acetylated pine specimen's time to ignition was reduced by 33% in comparison with reference wood. Average moisture content (MC) of conditioned reference wood samples was 11% but acetylated pine specimens MC was 1.5%. It was in contrary to results of reaction to fire tests with ash wood (Morozovs and Bukšāns 2009 a, b).

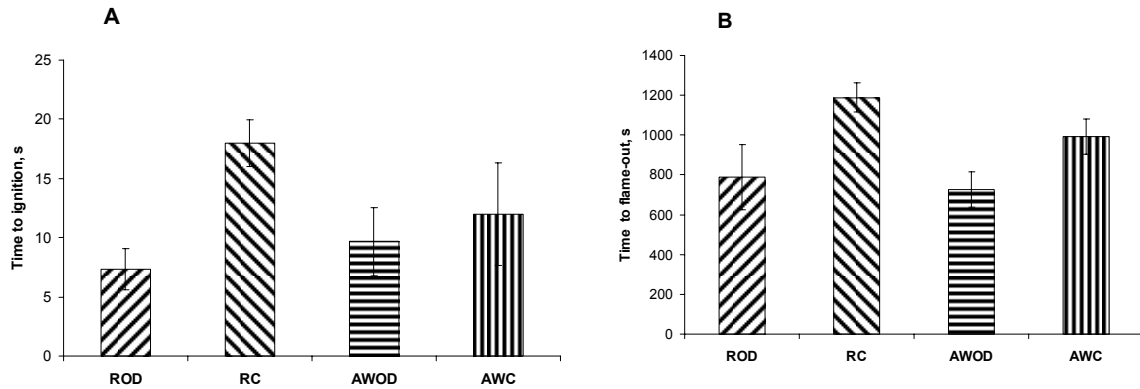


Figure 4: Time to ignition (A) and time to flame-out (B) of acetylated and reference wood ROD – oven-dried reference wood; RC – conditioned reference wood; AWOD – oven-dried acetylated wood; AWC – conditioned acetylated wood

Wood acetylation didn't alter shapes of the heat release rate (HRR) curves in comparison with reference wood but only shifted them to higher levels irrespective of the presence or absence of absorbed water or Impacts (I) were calculated according Eqn. 1.

$$I = (HRR_i - HRR_r) / HRR_r \tag{1}$$

Where HRR_i is HRR of wood sample whose impact is evaluated, HRR_r is HRR of reference. Moisture impact on reference wood reaction to fire was three times greater than with acetylated wood, although the EMC of reference wood was six times higher than of acetylated wood. Impact of moisture became less pronounced (only 65%) if compared between acetylated and reference wood

Impact of wood species and external heat flux

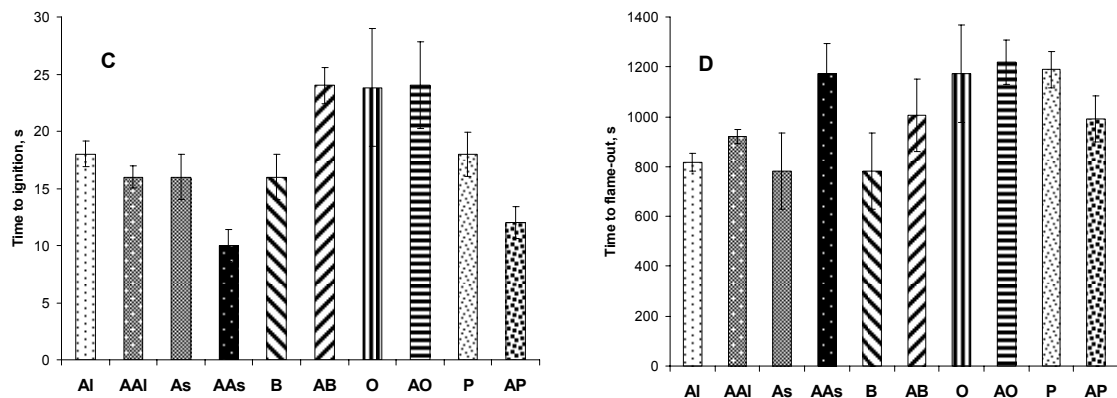


Figure 5: Effect of species on time to ignition (C) and time to flame-out (D) of acetylated and reference wood AI - alder, AAI - acetylated alder, As - aspen, AAs - acetylated aspen, B - birch, AB - acetylated birch, O - oak, AO - acetylated oak, P - pine, and AP acetylated pine wood

Conditioned acetylated and un-modified alder, aspen, birch, oak and pine wood samples were tested to check the influence of wood species on the reaction to fire in cone calorimeter tests (Figure 5). The impact of acetylation of different species of wood is sophisticated. Wood has a low thermal conductivity and the main increase of

temperature that is necessary to ensure pyrolysis is provided by radiation. The greater the external heat flux, the greater will be the exposed wood's surface and more intense wood thermal decomposition with volatiles and char formation. The oven dried pine wood and acetylated pine wood specimens were tested at different external heat flux in cone calorimeter to evaluate reaction to fire of both kinds of wood in changing heat flux that is characteristic for real fire conditions. Acetylation increases the time to ignition of oven-dried wood (Figure 6 E), but diminishes the flaming period (Figure 6 F)

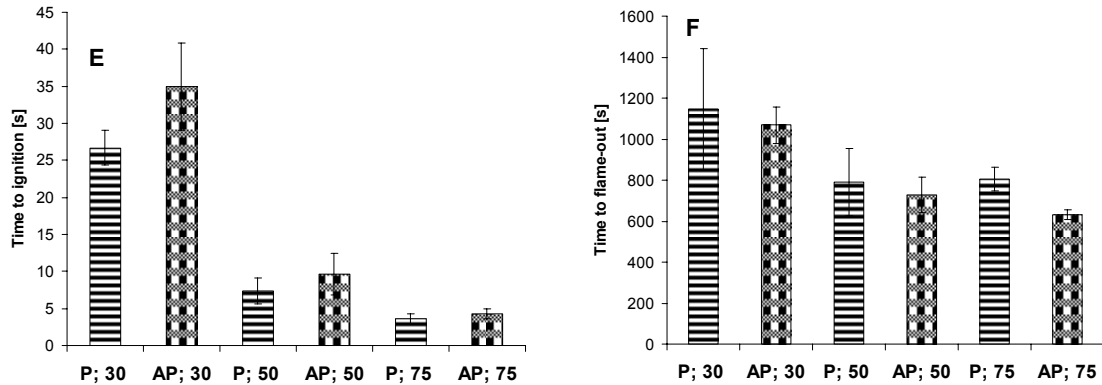


Figure 6: Effect of intensity of heat flux on the time to ignition (E) and time to flame-out (F) of acetylated and reference wood P – pine wood, AP acetylated pine wood; 30, 50 and 75 denoted heat flux 30 kW m⁻², 50 kW m⁻² and 75 kW m⁻².

Differences between ignition times of acetylated and reference wood were 31% at 30 kW m⁻²; 32% at 50 kW m⁻²; but diminish to 18% at 75 kW m⁻² heat flux. The high intensity of heat flux (75 kW m⁻²) creates higher temperature gradient in wood sample and causes disruption of chemical bonds more stable at lower heat fluxes that resulted in shorted period of sample burning with flame (Figure 6 F).

Impact of acetylation on production of smoke

Smoke is high risk factor that is reason for many lethal results, because it prevents individuals to orientation in smoke space and decreases possibility to escape in case of fire. Smoke optical density measured as smoke extinction area SEA at three rates of heat flux from acetylated pine wood was less than from un-modified one (Figure 7). Acetylated wood has decreased SEA by 41% at 30 kW m⁻²; by 12% at 50 kW m⁻²; and by 7% at 75 kW m⁻² heat flux. Total smoke release from pine wood area unit of acetylated wood is greater than from natural wood because of small difference of produced smoke optical density and the greater density of acetylated wood. Acetylated and un-modified pine wood showed higher smoke production in comparison with hard wood species. Acetylation decreases smoke optical density by 64% for alder wood, by 84% for aspen wood, by 41% for birch wood, by 52% for oak wood, but only by 3% for pine wood in comparison with references of each species (Figure 8). These data are obtained when conditioned according EN 13238:2002 specimens were used in cone calorimeter tests with 50 kW m⁻² heat flux.

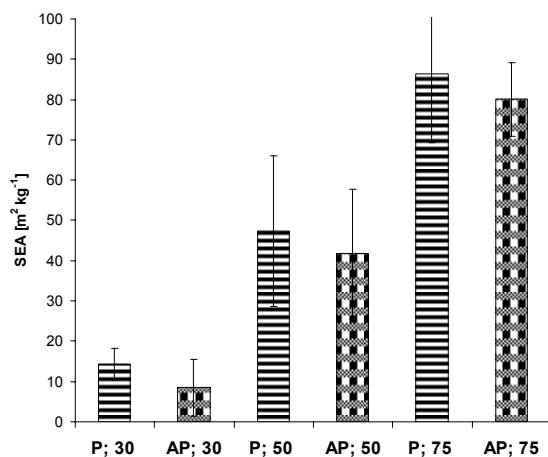


Figure 7: Influence of wood acetylation on smoke density at three levels of external heat flux. Designations the same as on Figure 6

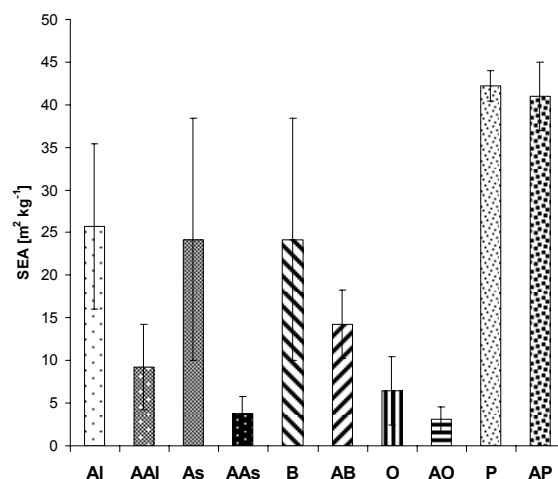


Figure 8: Influence of wood species and acetylation on smoke production at 50 kW m⁻² heat flux. Designations the same as on Figure 5

CONCLUSIONS

Wood acetylation has negative influence on reaction to fire of most parameters of reaction to fire with exception of ignition time and smoke production. Heat release of acetylated wood is greater than un-modified one. Acetylation impact on fire performance of pine (*Pinus sylvestris* L) wood is less pronounced than of hardwoods. Water sprinklers or fire resistant membranes could be recommended to protect wood constructions against heat radiation in case of fire. Acetylated wood has higher durability in moist conditions and for this reason is recommended for such uses that reduce fire risk.

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Photo-bleaching of Acetylated Wood

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Keywords: Acetylation; Colour; DRIFT spectroscopy; Photobleaching; Wood

ABSTRACT

This paper deals the photobleaching of acetylated wood. The acetylated spruce wood was irradiated by artificial sunlight emitted from xenon lamp with covering several kinds of band-pass filter. The lightness (L^*) of acetylated wood increased with integral irradiance. The chroma (ΔC^*) decreased by light-irradiation with wavelength from 430 nm to 500nm. However, the light-irradiation including ultraviolet ray region made it decrease after increase with integral irradiance. The visible light made hue angle (h°) increase, however the ultraviolet ray made it decrease. The lignin degradation and the production of carbonyl groups were observed by light-irradiation including ultraviolet ray. However, no remarkable changes in IR spectra were observed by visible light irradiation. Photobleaching of acetylated wood was caused by mainly visible light without modifying the IR spectra of lignin.

INTRODUCTION

It is well-known that the colour of wood surface changes to yellow by light-irradiation (Chang and Cheng 2001, Chang *et al.* 2000, Mitsui 2004, Müller *et al.* 2003, Ohkoshi 2002, Ohkoshi and Saijo 2001, Ota *et al.* 1996, 1997, Pandey 2005, Tolvaj and Faix 1995). It is reported that acetylation of wood improves not only its dimensional stability because the hydroxyl groups in cellulose are substituted to acetyl function (Evans *et al.* 2000, Hill and Jones 1996, 1999, Hill and Ormondroyd 2004, Sander *et al.* 2003), but also its colour stability against exposure to light (Ohkoshi 2002, Ota *et al.* 1996, 1997). It is clear in previous reports that the lightness (L^*) of acetylated wood increases by light-irradiation (Ohkoshi 2002, Ota *et al.* 1996, 1997). However, there are no reports on the detail discussion about that phenomenon. On the photo-thermal treatment of acetylated wood, the L^* increased more than that of unacetylated photo-thermally treated wood by exposure to light (Mitsui and Tolvaj 2004, 2005). Moreover, acetylation was applied to coloured wood by photo-thermal treatment, however, the light-irradiation after acetylation made L^* increase more than that of unacetylated one (Mitsui and Tolvaj 2004). As above, it is doubtful that acetylation is available to improve colour stability of all kinds of wood. Recently some researchers have discussed the effect of wavelength to photodegradation. Chang *et al.* (2000) and Chang and Cheng (2001) showed that the appearances of heartwood of Japanese cedar were redder than unirradiated wood after exposure to light of wavelengths above 600 nm. Mitsui (2004) showed that the chromaticness coordinate a^* which indicates reddish of six species of wood was minimal when irradiated at wavelengths longer than 500 nm, while the chromaticness coordinate b^* which indicates yellowish of them was minimal when irradiated at wavelengths longer than 440 nm. Kataoka *et al.* (2007) reported that blue light (434 - 496 nm) caused bleaching wood without significantly modifying the IR spectra of lignin. Yamamoto *et al.* (2007) examined several wood species and showed

that light-coloured wood specimens ($L^* > 70$, $a^* < 8$) underwent photodarkening and photobleaching when exposed to light in the UV and visible range, respectively. In this study, the experimental on light-irradiation using some kinds of band-pass filter was carried out to verify the photo-stability of acetylated wood, and the changes in colour and IR spectra were discussed.

EXPERIMENTAL

Materials

The species using in this study was Sitka spruce (*Picea Sitchensis*) having lumber 50 mm × 10 mm × 1 mm in longitudinal, tangential, and radial direction, respectively. Before acetylation, all the specimens were extracted in ethanol for 32 hours using Soxhlet apparatus and dried in vacuum at 40 °C.

Acetylation

The oven-dried specimens were treated with acetic anhydride in the liquid phase without a catalyst for 6 hours at 140 °C. At the end of the reaction, the specimens were extracted in ethanol for 16 hours using Soxhlet apparatus to remove unreacted reagent and dried in vacuum at 40 °C. The weight percent gain by acetylation was 22.80 ± 0.70 %.

Colour measurement

The colour of surface of specimens was measured with colourimeter (SE-2000: Nippon Denshoku Industries Co. Ltd., Japan). The sensor head was 6 mm in diameter. Measurements were made using a D₆₅ illuminant and a 10° standard observer. The tristimulus value X, Y, and Z of all specimens were obtained from the colourimeter. The CIELAB colour parameter (L^* , a^* , and b^*) were then computed, and the difference in the lightness (ΔL^*) and chroma coordinates (Δa^* and Δb^*), colour difference (ΔE^*), chroma (C^*), and hue angle (h°) were calculated using following formulae:

$$\begin{aligned}\Delta L^* &= L_a^* - L_b^* \\ \Delta a^* &= a_a^* - a_b^* \\ \Delta b^* &= b_a^* - b_b^* \\ \Delta E^* &= \sqrt{(\Delta L^*)^2 + (\Delta a^*)^2 + (\Delta b^*)^2} \\ C^* &= \sqrt{(a^*)^2 + (b^*)^2} \\ h^\circ &= \tan^{-1} \frac{b^*}{a^*}\end{aligned}$$

where the subscript a and b indicate the value after and before treatment, respectively. Table 1 shows the colour parameter of specimens before and after acetylation.

Table 1: Colour parameter of spruce wood before and after acetylation

Acetylation	L^*	a^*	b^*	C^*	h°
Before	61.64 ± 2.28	9.17 ± 0.96	28.78 ± 1.45	30.22 ± 1.36	72.29 ± 2.04
After	61.21 ± 2.10	5.01 ± 0.55	23.62 ± 1.58	24.15 ± 1.63	78.03 ± 0.86

IR measurement

IR measurement was performed using spectrometer (FT/IR-4200: JASCO Co. Ltd., Japan) equipped with a diffuse reflectance unit (DR-81: JASCO Co. Ltd., Japan). The resolution was 4 cm⁻¹ and 64 scans were averaged. After baseline correction between

1850 cm^{-1} and 850 cm^{-1} , the height of the band at 1161 cm^{-1} due to C-O-C stretching in polysaccharide was used as an internal standard (Ohkoshi 2002).

Light-irradiation

Light-irradiation was carried out with a xenon lamp at 63 °C (black panel temperature) and 50%RH for up to 1000 hours in a commercial chamber (SX-75: Suga Test Instruments Co. Ltd., Japan). Specimens were covered with seven kinds of band-pass filter (UTVAF-50S-34U: Sigma Koki Co. Ltd., Japan; MZ400, MZ430, MZ460, MZ500, MZ530, and MZ560: Asahi Spectra Co. Ltd., Japan). Fig. 1 and 2 show the spectral distribution of xenon lamp supplied by the lamp producer, and the transmittance curves of seven filters, which were measured by UV/VIS spectrometer (V-560: JASCO Co. Ltd., Japan), before and after light-irradiation, respectively. The peak width at half height of MZ series of band-pass filter was 10 nm.

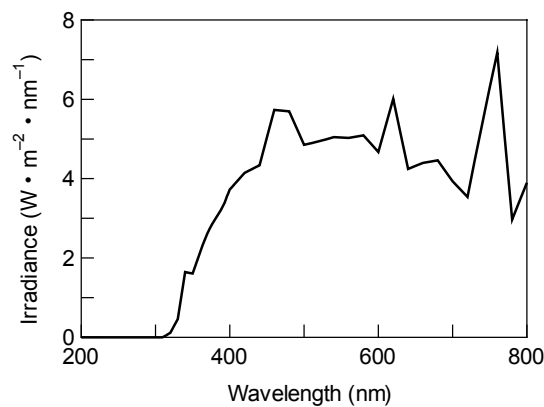


Figure 1: Spectral distribution of xenon lamp supplied by the lamp producer.

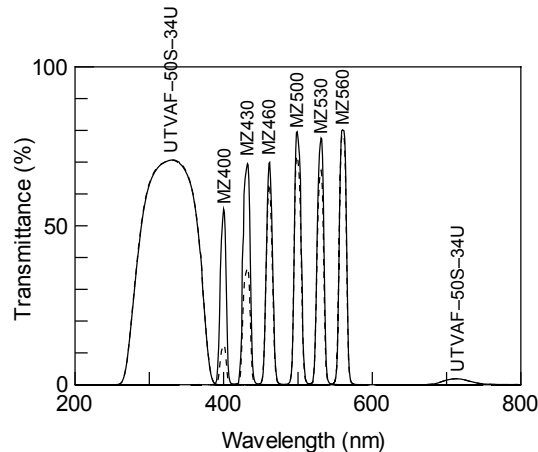


Fig. 2. Transmittance curve of band-pass filters before and after light-irradiation. :before light-irradiation, :after light-irradiation for 1000 h.

RESULTS AND DISCUSSION

Changes in colour

In the region between 200 nm and 800 nm, the integral irradiance Q (Jm^{-2}) irradiated to the sample surface was calculated by the following equation;

$$Q = \int_0^t \int_{200}^{800} \left(E_{\lambda} \times \frac{(1 - \alpha t) \times T_{\lambda}}{100} \right) d\lambda dt$$

where E , T , t , λ , and α indicate spectral irradiance ($\text{Wm}^{-2}\text{nm}^{-1}$), transmittance (%) of band-pass filter, time (s), wavelength (nm), and degradation rate (s^{-1}) of band-pass filter, respectively. The degradation rate α of band-pass filter was calculated by $\frac{T_{t=0h} - T_{t=1000h}}{T_{t=0h}} \times \frac{1}{60 \times 60 \times 1000}$ (s^{-1}), and those of UTVAF-50S-34U, MZ400, MZ430, MZ460, MZ500, MZ530, and MZ560 were 1.218×10^{-10} , 2.148×10^{-7} , 1.340×10^{-7} , 2.623×10^{-8} , 2.642×10^{-8} , 3.659×10^{-8} , and 5.507×10^{-9} , respectively.

Fig. 3(a) to (c) shows the relationship between ΔL^* , ΔC^* , h° and integral irradiance Q , respectively. The ΔL^* at all wavelength increased with integral irradiance. The changes in ΔL^* were regressed as $a \times \log Q + b$, and Table 2 shows the regression curve and correlation coefficient (r). When the entire wavelength was irradiated without band-pass filter (\bullet in Fig. 3) or only the region of ultraviolet (\circ) was irradiated to the specimens, the value of gradient a of regression curve were relatively small. However, when the visible light over 400 nm (\blacksquare) was irradiated, the values of gradient a were remarkably greater, and it maximized at 460 nm (\blacktriangle). At wavelength over 500nm, they decreased with wavelength. It was thought that increment of ΔL^* of acetylated wood by light-irradiation was mainly caused by visible light.

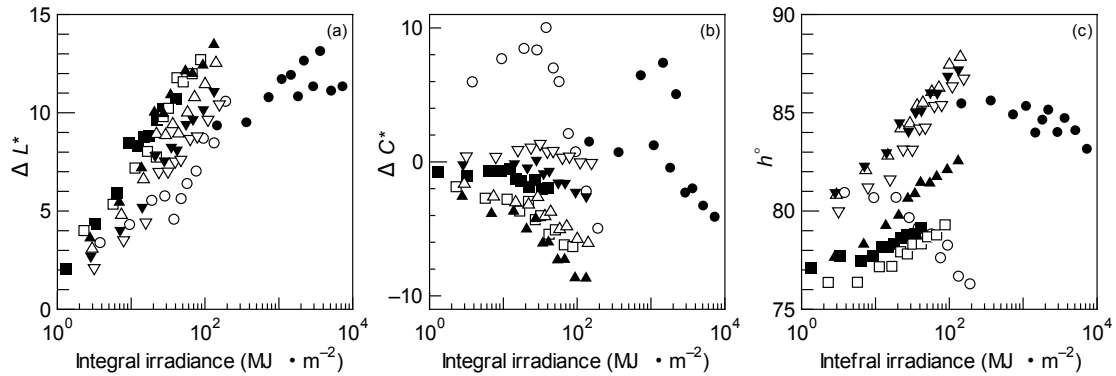
The ΔC^* is the difference between C^* of specimen after light-irradiation and that of acetylated specimens. The irradiation at 430 nm (\square), 460 nm (\blacktriangle), and 500 nm (\square) made ΔC^* decrease. The decrement of ΔC^* means that the colour of specimens changes to chromatic. Little changes of ΔC^* were observed by the light-irradiation at 400nm (\blacksquare), 530 nm (\blacktriangledown), and 560 nm (\square). However, in the case of the light-irradiation at ultraviolet region, after ΔC^* increased with integral irradiance, it decreased drastically.

The hue angle (h°) increased with integral irradiance, which means that the colour of specimens changed to yellowish in the case of light-irradiation in the region of visible light. However the light-irradiation in the region of ultraviolet made h° decreased, which means that the colour of specimens changed to reddish.

These results showed that both ultraviolet ray and visible light made the acetylated wood photobleach and visible light was more effective than ultraviolet ray. It was suggested that the mechanism of photobleaching of acetylated wood by ultraviolet ray differed from that by visible light.

Table 2: Regression curves ($a \times \log Q + b$) and correlation coefficients (r) calculated from the changes in ΔL^* .

Type of band-pass filter	Peak position of band-pass filter (nm)	Regression curve	r
UTVAF-50S-34U	340	$\Delta L^* = 3.81 \times \log Q + 0.22$	0.90**
MZ400	400	$\Delta L^* = 5.96 \times \log Q + 1.55$	0.99**
MZ430	430	$\Delta L^* = 5.94 \times \log Q + 1.03$	0.98**
MZ460	460	$\Delta L^* = 6.13 \times \log Q + 0.90$	0.98**
MZ500	500	$\Delta L^* = 5.61 \times \log Q + 0.36$	0.99**
MZ530	530	$\Delta L^* = 5.24 \times \log Q - 0.03$	0.99**
MZ560	560	$\Delta L^* = 5.13 \times \log Q - 0.80$	0.99**
without band-pass filter		$\Delta L^* = 1.58 \times \log Q + 6.17$	0.69*



**Figure 3: Relationship between colour parameter and integral irradiance Q . (a) ΔL^* , (b) ΔC^* , (c) h° .
 ●: without band-pass filter, ○: with UTVAF-50S-34U (340 nm), ■: with MZ400 (400 nm), □: with MZ430 (430 nm), ▲: with MZ460 (460 nm), □: with MZ500 (500 nm), ▼: with MZ530 (530 nm), □: with MZ 560 (560 nm).**

Changes in IR spectra

Fig. 4 shows the changes in IR spectra by light-irradiation without band-pass filter (a), with UTVAF-50S-34U (340 nm) (b), and with MZ400 (400 nm) (c). When acetylated wood was irradiated without any filter, the peak at 1510 cm^{-1} assigned to aromatic skeletal originated from lignin decreased with light-irradiation time and it disappeared at 250 hours of light-irradiation time as shown in Fig. 4(a). According to the report by Ohkoshi (2002), there were little changes in the aromatic skeletal due to lignin by light-irradiation for 100 hours. The experimental was carried out by using xenon lamp having irradiance of $1.11\text{ MJ}\cdot\text{m}^{-2}\cdot\text{h}^{-1}$ at wavelengths of 300 - 700 nm. The irradiance at wavelengths of 300 - 700 nm in this experimental was $5.83\text{ MJ}\cdot\text{m}^{-2}\cdot\text{h}^{-1}$ by calculating from Fig. 1. That is, the light-irradiation for 100 hours of his experiment corresponds to that for 19 hours in this study. The peak at 1604 cm^{-1} assigned to C=C stretching of aromatic ring due to lignin also decreased with light-irradiation time. These results indicate that lignin in the acetylated wood degrades by exposure to light. On the other hand, the peaks at 1645 cm^{-1} and 1702 cm^{-1} assigned to C=O stretching in conjugated system and unconjugated carbonyl groups, respectively, increased with irradiation time. The peak at 1762 cm^{-1} assigned to carbonyl groups increased by acetylation and it increased more by light-irradiation. The peak around 1740 cm^{-1} assigned to carbonyl groups consists of two sub-bands around 1710 cm^{-1} and 1760 cm^{-1} , and the former is more low-molecular-weight hydrophilic compounds than the latter (Mitsui *et al.* 2004, Tolvaj and Faix 1995). In previous reports (Mitsui *et al.* 2004, Tolvaj and Faix 1995), the discrimination of two-bands was appeared by the calculation of different spectra. It was thought that two peaks were revealed since the peak of carbonyl group at higher wavelength sharpened by acetylation and shifted to higher wavelength by exposure to light. In the case of light-irradiation with band-pass filter which transmits only ultraviolet region (Fig. 4(b)), the tendency was almost same as the case of light-irradiation without any band-pass filter (Fig. 4(a)). However, in Fig. 4(b) the peak around 1710 cm^{-1} was not clear and overlapped with the peak around 1760 cm^{-1} . In the case of light-irradiation with band-pass filter at 400 nm, no remarkable changes could be observed by light-irradiation (Fig. 4(c)).

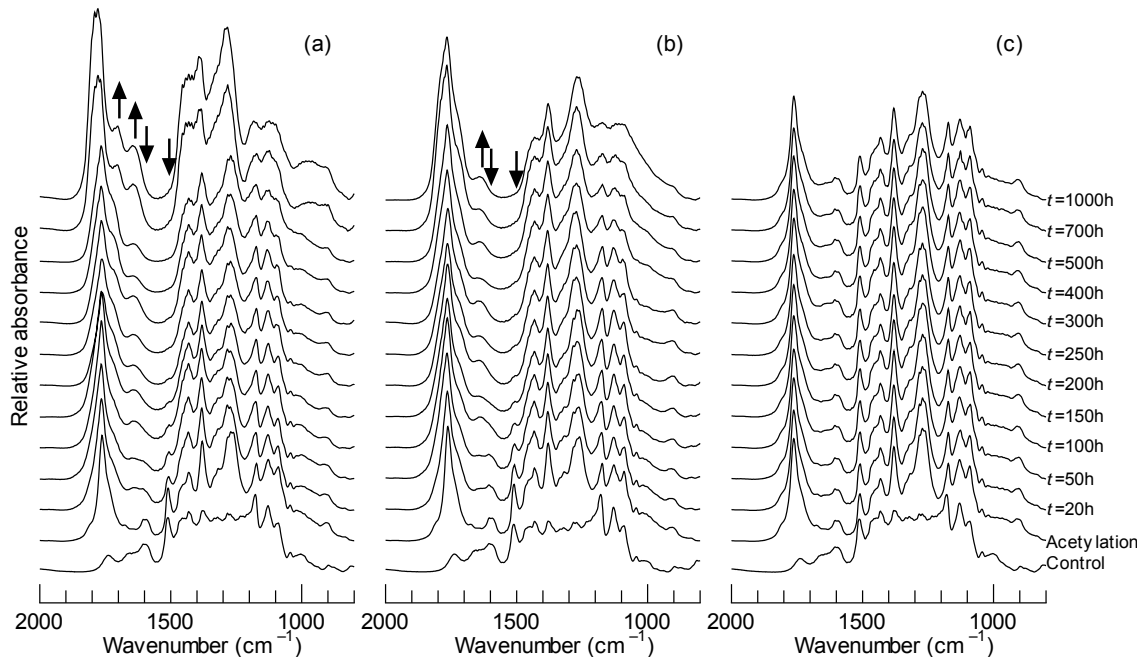


Figure 4: Changes in IR spectra by light-irradiation. (a) without band-pass filter, (b) with UTVAF-50S-34U (340 nm), (c) with MZ400 (400 nm).

Fig. 5 shows the relationship between integral irradiance and the ratios of absorbance A_{σ} after light-irradiation to before irradiation, V_{σ} . That is,

$$V_{\sigma} = \left\{ \frac{\left(\frac{A_{\sigma}}{A_{1161}} \right)_{After}}{\left(\frac{A_{\sigma}}{A_{1161}} \right)_{Before}} \right\}$$

V_{1510} and V_{1740} indicate the photodegradation of lignin and the production of carbonyl groups by light-irradiation, respectively. V_{1510} of specimens uncovered and covered with UTVAF-50S-34U decreased with integral irradiance. V_{1740} of specimens uncovered and covered with UTVAF-50S-34U increased with integral irradiance. These results agree with previous reports (Kataoka *et al.* 2007, Müller *et al.* 2003, Ohkoshi 2002, Ohkoshi and Saijo 2001, Pandey 2005, Tolvaj and Faix 1995, Yamamoto *et al.* 2007). On the other hand, no remarkable changes in V_{1510} were observed for specimens covered with MZ430, MZ460, MZ500, MZ530, and MZ560, that is, filters which do not transmit ultraviolet ray. Equally, there were little changes in V_{1740} for specimens to which ultraviolet ray was not irradiated. These results show that the photodegradation of lignin and the production of carbonyl groups by light-irradiation are caused by only ultraviolet ray. Moreover, photobleaching of acetylated wood is caused by mainly visible light without modifying the IR spectra of lignin.

CONCLUSIONS

In this study, the photobleaching of acetylated wood was discussed based on the experimental using band-pass filters. The ΔL^* of acetylated wood increased with integral irradiance. The ΔC^* decreased by light-irradiation with wavelength from 430 nm to 500nm. However, the light-irradiation including ultraviolet ray region made it decrease after increase with integral irradiance. The h° increased by visible light, on the other hand, it decreased by the ultraviolet ray. From the results of IR spectra, the lignin

degradation and the production of carbonyl groups were observed by light-irradiation including ultraviolet ray. However, no remarkable changes in IR spectra were observed by visible light irradiation. Photobleaching of acetylated wood was caused by mainly visible light without modifying the IR spectra of lignin.

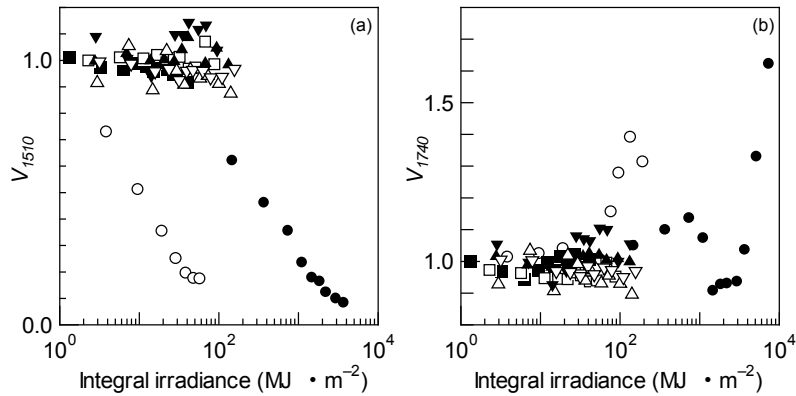


Figure 5: Relationship between integral irradiance and the ratios of absorbance A_{σ} after light-irradiation to before irradiation (V_{σ}). (a) V_{1510} , (b) V_{1740} . ●: without band-pass filter, ○: with UTVAF-50S-34U (340 nm), ■: with MZ400 (400 nm), □: with MZ430 (430 nm), ▲: with MZ460 (460 nm), □: with MZ500 (500 nm), ▼: with MZ530 (530 nm), □: with MZ560 (560 nm).

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Production of Acetylated Wood Fibre: Part 1: Refining Acetylated Chips; Part 2: Exploding Acetylated Chips; Part 3: Acetylation of Chips in a Refiner

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Keywords: Wood, chips, acetylation, refiner, explosion, fibre length, equilibrium moisture content, decay resistance, dimensional stability

ABSTRACT

Fibreboards made using acetylated fibre have the highest dimensional stable and decay resistance as compared to other composites made using larger wood geometries (i.e. particleboard, flake board and chip board) and much higher compared to acetylated solid wood. Several methods have been published to produce acetylated fibre for the production of acetylated fibreboard, however, there are problems handling fibre and feeding it into a reactor. Chips are much easier to handle and can be produced in a wide variety of sizes and shapes. This paper will report on three new methods to produce acetylated fibre starting from chips. In the first method, chips of various sizes are first acetylated to the desired level of acetylation and then refined. The results show that soaking the chips in water or steaming them helps soften them before refining. Also the level of acetylation increases with decreasing chip size, however, it is evident that new hydroxyl sites are being exposed as the acetylated chips are refined. In a second method, acetylated chips are reduced to fibre using explosion technology. The disadvantage of this method is that both single fibres and fibre bundles are generated and the fibre bundles need to be refined further. In a third approach, the acetylating agent is present when the chips are reduced to fibre in a refiner substituting all hydroxyl groups as they became exposed. Acetylating chips in a refiner is done using one of two methods: a one step procedure and a two step. In the one step procedure, the chips are fed into the refiner, along with hot acetic anhydride and the chips and hot anhydride remain in the refiner until the desired weight gain has been achieved. In the two step process, the chips are first fed into a reactor along with hot acetic anhydride and held in the reactor until the desired level of acetyl is reached and then the mixture of chips and hot anhydride is conveyed into the refiner. A final reactor can be added after the refiner to complete the acetylation process if needed. Acetyl weight gain, a visual fibre length distribution and equilibrium moisture content were determined at each step in the three methods and this EMC value was correlated with dimensional stability and decay resistance.

INTRODUCTION

Almost all past research on wood acetylation starts and ends with the same geometry. That is, solid wood is acetylated to produce acetylated solid wood, flakes are acetylated to produce acetylated flakeboard or fibre is acetylated to make acetylated fibreboard. Early research showed that some of the hydroxyl groups in solid wood that could be acetylated are not accessible to reactive chemical so acetylated solid wood contains some hydroxyl groups that are unreacted (Rowell and Rowell 1989). Many of the

hydroxyl groups in chips are acetylated but even with the smallest chips, a few of the hydroxyl groups are still unsubstituted. Most of the hydroxyl groups in wood fibre are accessible to reactive chemical so more hydroxyl groups are covered in acetylated fibre as compared to acetylated chips. Even acetylated fibre has a few hydroxyl groups not substituted so the smaller water molecule can still find sites to hydrogen bond to.

This research is directed to producing acetylated fibre using several new approaches. In the first, acetylated chips of different sizes are acetylated, then softened by water soaking or steam or microwave and then refined. The equilibrium moisture content (EMC), visual fibre size distribution and acetyl weight gain were determined. In the second approach, acetylated chips are exploded using a lab scale model of the Masonite gun in West Chicago, IL. In the final approach, chips are acetylated in a refiner using one of two techniques: reaction and refining in one step or reacting and refining in two connected steps. All of the acetylation reactions were done using the simplified procedure, i.e. no catalyst or cosolvent (Rowell *et al.* 1986).

EXPERIMENTAL

Part 1: Refining Acetylated Chips

Oven dried southern pine chips of different sizes were acetylated using acetic anhydride at a reaction temperature of 140°C. The largest chip was 7.5 x 5 x 1.5 cm (length x width x thickness) and the smallest was 2 x .25 x .25 cm. The different size chips were acetylated at 140°C for various times and the weight gain recorded. EMC, at 90% relative humidity (RH) and 27°C, was determined on each acetylated chip size. Chips were then: (1) refined directly, (2) soaked in cold water overnight, (3) steamed for 4 hours or (4) soaked in water overnight and then heated using microwave energy for 15 minutes. The processed chips were then fed into a small double disk atmospheric refiner. EMC, visual fibre size determination and acetyl content were determined on each type of isolated acetylated fibre.

Part 2: Exploiting Acetylated Chips

Oven dried southern pine chips were acetylated using acetic anhydride alone at 140°C for two hours. The average chips were 2 x 1 x .5 cm (length x width x thickness). The chips were washed in water and oven dried. The weight percent gain was 21.7. The chips were placed under pressure (250 - 359 psi) in a laboratory scale Masonite exploder located in West Chicago, IL and the pressure quickly released to atmospheric pressure causing the chips to explode into fibre bundles and single fibres. EMC, at 90% relative humidity (RH) and 27°C, and visual fibre size distribution were determined on the isolated acetylated fibre and fibre bundles.

Part 3: Acetylation of Chips in a Refiner

Experiments were started in 2003 to explore the concept of acetylating wood chips combining the reaction and refining steps into one operation. There is no prior art on acetylating wood while changing the geometry at the same time. This can be done in one or two steps: In the single process, chips are reduced to the final geometry in the presence of hot acetic anhydride in the refiner while in a two step process, the chips are acetylated in a pre-reactor and then conveyed to a refiner in the presence of hot acetic anhydride and reduced to fibre.

In the single step process, the dried chips and acetic anhydride are placed in a refiner at 140°C and reacted and refined at the same time. Since, however, reducing chips to fibre in a refiner has a very short residence time in the reducing equipment, a two step process can be done using a pre-reactor to increase the acetyl content to nearly the desired level and the conveying the chips and reacting chemical directly to the refiner to reduce the acetylated chips to acetylated fibre in the presence of hot acetic anhydride.

Single Step Process

Southern pine chips are dried to a moisture content of less than 10% placed in an atmospheric Asplund Defibrator D connected to a 20 hp Baldor Industrial motor. Acetic anhydride is introduced into the defibrator along with the chips (2 x 1 x 1 cm) and the temperature raised to 140°C. The gap between the defibrator blades and the wall is 0.7 mm. The door is sealed and the defibrator is held at 140°C run at 1700 rpm for different lengths of time. Excess anhydride and by-product acid were removed, the acetylated fibre washed with water and dried in an oven at 105°C. EMC, at 90% relative humidity (RH) and 27°C, acetyl weight gain and visual fibre size distribution were determined on the isolated acetylated fibre.

Two Step Process

Southern pine chips (2 x 1 x 1 cm) are dried to a moisture content of less than 10% and conveyed to a reaction vessel at atmospheric pressure that is connected to a Sprout-Bauer double disc refiner. Acetic anhydride is introduced into the reaction vessel and the temperature raised to 140°C for different lengths of time. The acetylation reaction is continued until the desired level of acetylation is achieved. The acetylated chips and reaction mixture are then conveyed to the refiner and the acetylated fibre refined. Excess anhydride and by-product acid were removed using a hot gas or water washing. EMC, at 90% relative humidity (RH) and 27°C, visual fibre size distribution and acetyl content were determined on the starting chips and isolated acetylated fibre.

RESULTS AND DISCUSSION

Part 1: Refining Acetylated Chips

Figure 1 shows the various sizes of southern pine chips used in these experiments. The size given for each experiment is the average of all the chip sizes used in that experiment.



Figure 1: Southern pine chips of various sizes used for acetylation.

Table 1 shows the weight percent gain (WPG) of southern yellow pine chips of different sizes reacted at 140°C for various lengths of time. The largest chips take much longer to

reach a weight gain over 20%. Isolated fibre reacts the fastest and reaches the target WPG in about 45 minutes.

Table 1: Weight percent gain (WPG) of acetylated southern yellow pine chips of different sizes (140 °C) at different times

Chip size [cm] L x W x T	Weight Percent gain at: [minute]				
	15	30	45	60	120
7.5 x 5 x 1.5	10.4	13.6	16.7	18.2	20.2
5.5 x 3 x 1	11.3	14.7	16.8	19.2	20.8
3.5 x 2 x 1	12.6	14.8	17.1	19.3	20.9
2 x .25 x .25	13.8	15.2	18.3	20.6	21.8
Fibre	14.2	16.3	20.9	21.1	23.5

Table 2 shows the equilibrium moisture content (EMC) of the acetylated chips reacted in Table 1. The control chips have an EMC of 17.7, the largest chips 7.1 which decreases to 3.6 in the acetylated fibre. These results support earlier findings that some hydroxyl groups are not accessible to acetic anhydride as the chip size increases.

Table 2: Equilibrium moisture content of control and acetylated chips

Chip size [cm]	WPG	EMC (90%, 27 °C)
7.5 x 5 x 1.5	20.2	7.1
5.5 x 3 x 1	20.8	6.9
3.5 x 2 x 1	20.9	6.9
2 x .25 x .25	21.8	6.2
5.5 x 3 x 1	0	17.7
Fibre	23.5	3.6

Table 3 shows the EMC of fibre after refining the control and acetylated chips shown in Table 2. While the WPG does not change, the EMC of the refined fibre is higher in the fibre as compared to the unrefined chip. More evidence of hydroxyl groups not acetylated during the initial reaction.

Table 3: Equilibrium moisture content of fibre after refining control and acetylated chips

Chip size [cm]	WPG	EMC (90%, 27 °C)
7.5 x 5 x 1.5	20.2	9.3
5.5 x 3 x 1	20.8	8.6
3.5 x 2 x 1	20.9	8.4
2 x .25 x .25	21.8	7.2
5.5 x 3 x 1	0	17.7

It was observed after the refining process that the majority of the fibres coming from acetylated chips ranged in length from very short to dust. In an attempt to increase the fibre length after refining, several methods were used to soften the acetylated chip to decrease the fibre damage during refining. Table 4 shows the visual distribution of fibre after refining using no treatment (NT), soaking in water (WO), 4 hour steaming (S4) and water soaking following by microwave heating (W-MW). The data clearly shows that softening the acetylated chips before refining does result in an average increase in fibre length and a smaller amount of short fibre. The best results were obtained by steaming or water soaking followed by microwave heating.

Table 4: Visual fibre size distribution of refined control and acetylated chips

Chip size [cm] L x W x T	WPG	Fibre size distribution (%LF/SF)			
		NT	WO	S4	W-MW
7.5 x 5 x 1.5	20.2	40/60	50/50	60/40	60/40
5.5 x 3 x 1	20.8	40/60	45/55	55/45	60/40
3.5 x 2 x 1	20.9	50/50	45/55	55/45	60/40
2 x .25 x .25	21.8	50/50	55/45	55/45	60/40
5.5 x 3 x 1	0	80/20	80/20	80/20	85/15

LF =long fibre, SF = short fibre or dust, NT = No treatment, WO = Water soak, S4 = Steam 4 hours, W-MW = Water soak then microwave heating.

Part 2: Exploiting Acetylated Chips

Table 5 shows the data from exploding control and acetylated chips. Mainly single fibres resulted by exploding control chips but more fibre bundles were observed in the explosion of acetylated chips. There was only a small amount of dust-like particles in both the exploded control and acetylated fibres. The EMC increased slightly after explosion in both the control and acetylated samples.

Table 5: Equilibrium moisture content and visual fibre size distribution of exploded control and acetylated chips

Chip Type	EMC (90%, 27 °C) (before)	Fibre size distribution (% F/FB)	EMC (90%, 27 °C) (after)
Acetylated chips	8.7	60/40	9.7
Control chips	16.4	80/20	17.2

WPG = 21.7, F = Fibre, FB = Fibre bundles

Part 3: Acetylation of Chips in a Refiner

Single Step Process

The equipment used in the single step process is shown in Figures 2 and 3. The WPG resulting from acetylation in the defibrator is shown in Table 6. Comparing Table 6 with Table 1, the chips are acetylated faster in the refiner, however, Table 7 shows that due to the long contact with the defibrator blades during the acetylation reaction, the resulting fibre is very short. This finding lead to a two step process where the reactions was done first and then the acetylated chips were refined in contact with the hot reaction media.

Table 6: Weight percent gain (WPG) of acetylated southern yellow pine chips at different times (140 °C)

Weight Percent gain at [minute]			
15	30	45	60
15.6	17.2	20.2	21.6

Table 7: Equilibrium moisture content and visual fibre size distribution of fibre after refining acetylated chips

WPG	EMC (90%, 27 °C)	LF/SF
20.2	3.6	5/95
21.6	3.3	2/98

LF =long fibre, SF = short fibre or dust



Figure 2: Asplund Defibrator D



Figure 3: Asplund Defibrator with 0.7 mm gap

Two Step Process

Table 8 shows the data from the two step process. The chips are first acetylated to different WPG's and then transferred to the refiner along with the hot reaction media. After the refining step, the EMC was determined and a visual size distribution was determined. The chips reacted to 20.1 WPG had an EMC of 4.9 and the fibre mainly consisted of long fibre. This showed less fibre damage than was observed in the single step refining process.

Table 8: Weight percent gain, equilibrium moisture content and visual fibre size distribution of fibre after refining acetylated chips

Reaction Time [min]	WPG	EMC (90%, 27 °C)	LF/SF
15	13.2	11.2	80/20
30	16.6	8.3	75/25
45	18.9	6.3	70/30
60	20.1	4.9	60/40

LF =long fibre, SF = short fibre or dust

Table 9 shows data from past research showing the correlation between EMC and dimensional stability (antishrink efficiency ASE) and weight loss after a 12 week ASTM standard soil block test with both a brown- and white-rot fungi (Rowell 2006). All past data indicate that if the final EMC of the acetylated fibre is below about 7, composites made using that fibre will have a very high dimensional stability and will be resistant to attack by brown- and white-rot fungi.



Figure 4: Sprout-Bauer double disc, pressurized refiner

Table 9: Correlation between EMC and dimensional stability and decay resistance of fibreboards made from control and acetylated southern yellow pine fibre

WPG	EMC	ASE	Weight loss (%)	
			Brown-rot	White-rot
0	17.7	-	61.3	7.8
12.3	10.8	61.9	6.7	2.6
15.8	8.9	77.1	3.4	<2
17.1	7.3	84.8	<2	<2
20.8	3.8	94.7	<2	<2

EMC at 90% RH, 27 °C, ASE = antishrink efficiency, 12 week soil block ASTM D 2017-71 test - Brown-rot fungus = *Gloeophyllum trabeum*, White-rot fungus = *Trametes versicolor*

CONCLUSIONS

Several new methods have been explored for the production of acetylated fibre. The rate of acetylation depends on the size of the wood chips. As the chip size increased, the rate of acetylation decreased and the EMC of the refined acetylated fibre is slightly higher than the acetylated chips before refining. A large amount of very short fibres resulted from this method. Water soaking, steaming or water soaking followed by microwave heating before refining the acetylated chips reduces the amount of short fibres after refining. Exploding acetylated chips to fibre also reduces the amount of short fibres as compared to refining the acetylated chips directly. Reacting and refining in a single step results in acetylated fibre with a very low EMC but the fibres are very short. Reacting first and then refining in the reaction media results in a higher level of long fibre and a low EMC value. Another variation of this method might be to expand to a three step process where an added reaction step is added after refining. Both the two step and three step procedures would be done in a continuous process where the reactors and refiner are connected and chips/fibre conveyed by means of a plug screw or the like. Research is continuing on freeze drying and critical point drying of chips before acetylation to maintain a more open structure for reagent penetration as compared to oven drying. Research is also continuing on the design of a continuous reactor-refiner.

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Effect of Glutaraldehyde Modification on the Dynamic Water Vapour Sorption Behaviour of Scots Pine Wood

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Keywords: Cell wall, cross-linking, dynamic water vapour sorption, glutaraldehyde, hysteresis.

ABSTRACT

Scots pine (*Pinus sylvestris* L.) wood was modified with the crosslinking agent glutaraldehyde (GA) to weight percent gains of 0.5, 8.6, 15.5, and 21.0%, respectively. The modifying effects on the water vapour sorption properties were studied using a Dynamic Vapour Sorption apparatus. GA modification considerably reduced the equilibrium moisture content (EMC) of wood and the time taken to reach the EMC at each target relative humidity (RH). Increasing the GA concentration resulted in a lower EMC and shorter equilibrium sorption time. The modified wood exhibited a lower hysteresis with the increased GA concentration through the set RH range. Both the untreated and treated wood showed a higher moisture decrement in the adsorption run than its moisture increment in the desorption run in the RH range of 5-60%; however, in the RH range of 70-90% all tested samples presented higher moisture increments than moisture decrements in the isotherm run. The changes in the moisture sorption behaviour caused by GA treatment may be due to cell wall bulking (reducing void volume), hydroxyl groups deactivation (reducing the sorption sites), and cell wall polymer crosslinking (reducing the elasticity of cell wall).

INTRODUCTION

Chemical modification is one of the strategies to change the moisture sorption properties of wood primarily through the covalent bonding of chemicals with the hydroxyl groups of cell wall polymers or by depositing sterically fixed compounds, mainly of high molecular weight, in the cell wall (Hill 2006). As a result, the hygroscopic hydroxyl groups of cell walls are partly blocked and the nanopores (nanocapillaries) of cell walls are filled with the chemicals. Blocking of hydroxyl groups reduces the sorption sites to water and deposition of chemicals in the cell walls reduces the space for moisture thereby simultaneously making the cell walls drier and more dimensionally stable.

Glutaraldehyde (GA, pentane-1,5-dial) is a dialdehyde which can in principle react with four hydroxyl groups of the cell wall polymers and may thus be used as a crosslinking agent to modify wood. An aldehyde can react with one hydroxyl group to form a hemiacetal and with a second to produce an acetal. Whilst the hemiacetal formed is

susceptible to hydrolysis, the acetal bond is stable under both neutral and acidic conditions. The crosslinking reaction can be facilitated by heating the treated wood in the presence of catalysts (Yasuda and Minato 1994, Yasuda *et al.* 1994, Xiao *et al.* 2009). Treatments of Scots pine sapwood with glutaraldehyde and magnesium chloride as a catalyst were shown to cause a reduction of the EMC of up to 30%. The anti-swelling efficiency (ASE) at water saturation was 70% when the wood was treated to a weight percent gain (WPG) of approximately 20% (Xiao *et al.* 2009). Glutaraldehyde treatment reduced both the maximum swelling and shrinking, suggesting that both bulking and crosslinking occur within the wood cell walls (Xiao *et al.* 2010). Recently, dynamic vapour sorption (DVS) has been used to investigate the sorption properties of different natural fibers (Hill *et al.* 2009a), cotton fabric (Leisen *et al.* 2002), and Sitka spruce wood (Hill *et al.* 2009b). This DVS technique yields highly reproducible data and is able to provide accurate isotherms over a wide RH range (Hill *et al.* 2009a). The main objective of this study is to establish the effect of glutaraldehyde modification on the dynamic vapour sorption properties of wood by using a Dynamic Vapour Sorption apparatus. The changes of environmental RH and moisture content of wood were recorded, and then the sorption hysteresis between adsorption and desorption runs and moisture increment and decrement of wood at each given relative humidity were analyzed accordingly.

EXPERIMENTAL

Wood and chemicals

Wood blocks measuring 5 mm (longitudinally) x 20 mm (tangentially) x 20 mm (radially) were cut from the sapwood of Scots pine (*Pinus sylvestris* L.) boards. The modifying agent was a 50 wt% solution of glutaraldehyde (GA) supplied by BASF AG (Ludwigshafen, Germany). Magnesium chloride hexahydrate ($\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$) was used as catalyst.

Treatment of wood

Ten wood blocks were impregnated in aqueous acetate buffer solutions (0.1M, pH 4.5) of 0.4, 1.2, 2.0, 3.0 M glutaraldehyde and 12.5 wt% magnesium chloride (relative to the weight of glutaraldehyde), respectively, under vacuum conditions (100 mbar, 30 min) and pressure (10 bar, 1 h). After impregnation, excess treatment solution was blotted off the wood blocks with tissue paper and the wood blocks were air dried for one week. Subsequently, the specimens were pre-cured at 80°C (6 h) and then finally cured at 120°C (48 h). After conditioning (20°C, 65% RH) for 24 h, all the untreated and treated specimens were leached with daily changed tap water for 1 week to remove the unreacted glutaraldehyde and magnesium chloride and subsequently oven dried and weighed. The treated and leached samples ultimately attained the weight percent gains of 0.5%, 8.6%, 15.5%, and 20.9%, respectively. Untreated wood blocks served as control specimens. The untreated and treated wood blocks were ground into wood flour and passed through a 20 mesh sieve.

Determination of dynamic water vapour sorption

Isotherm analysis of wood flour was studied using a Dynamic Vapour Sorption apparatus (DVS Intrinsic, Surface Measurement Systems Ltd, London, United Kingdom) as previously reported (Hill *et al.* 2009^a). Wood flour prepared as above of ca. 20 mg was placed on the sample holder which is connected to a microbalance by a hanging wire and is located in a thermostatically controlled cabinet. The pre-set RH

increased in steps in the following sequence (0, 5, 10, 15, 20, 30, 40, 50, 60, 70, 80, 85, 90, and 95% RH), before decreasing to 0% RH in the reverse order. The sorption processes were run at a constant temperature of 25 °C over the full RH range. The instrument maintained a constant target RH until the sample moisture content change per minute (dm/dt) was less than 0.002% per minute over a ten minute period. In practice, this does not mean that it reaches a true equilibrium, but previous studies have established that this allows for obtaining EMC values within 0.1% of the true equilibrium value (i.e. infinite time). The running time, target RH, actual RH, sample mass were recorded throughout the isotherm run.

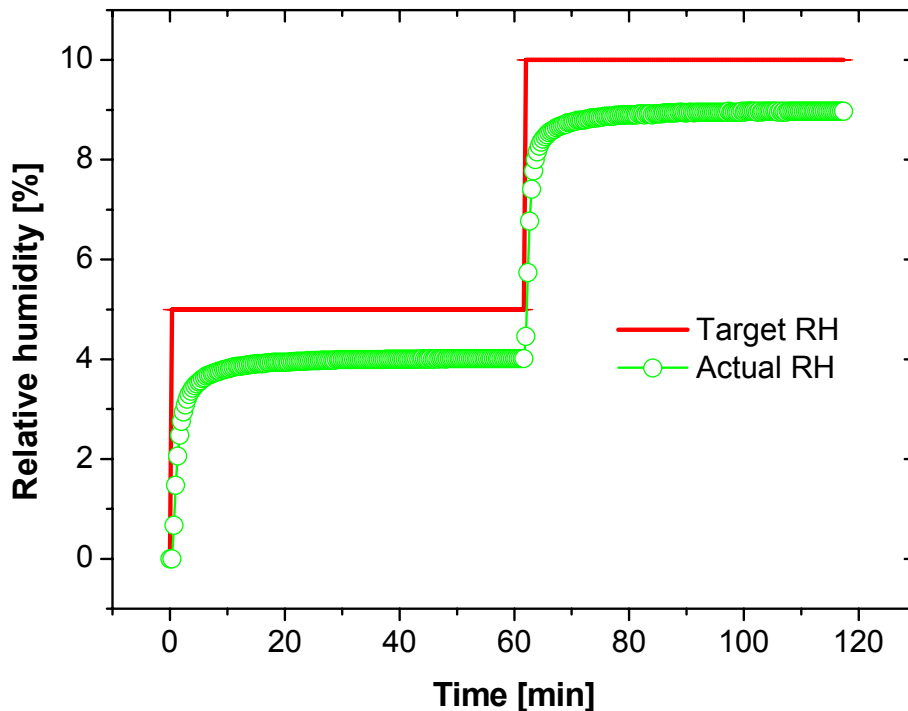


Figure 1: The changes of target relative humidity and actual relative humidity with the running time.

RESULTS AND DISCUSSION

Dynamic sorption behaviour of wood

The relative humidity (RH) did not promptly reach the set target RH as the RH control programme changed to next RH. It will take proximately 10 min to reach a constant RH approaching the target RH but with a minor deviation (Figure 1). The response of a wood sample to the change in the set RH produced an asymptotic curve approaching the equilibrium moisture content (EMC) after infinite time of exposure at a given RH (Figure 2). This has previously been explained with a plasticization mechanism of cell wall macromolecules with gradually increase of moisture content based on NMR studies. The NMR study of the sorption isotherm of cotton fabric has revealed that with the increase of RH over 35% some portion of cellulose hydroxyl groups become mobile due to the fast exchange between the sorbed water and the cellulosic –OH groups and/or plasticization and thus mobilization of some segments of cellulose matrix (Topgaard and Södermann 2001, Leisen *et al.* 2002). However, the plasticized –OH groups is only 30% of total cellulosic –OH groups at the 85% RH level because the other inaccessible –OH groups locate in the crystalline region of cellulose (Leisen *et al.* 2002). A plasticization effect of this type increases chain mobility and hence the swellability of

the cell wall. The capillary condensation also may occur in the higher RH range as the water vapour pressure increases with the increased RH and swelling of wood might also become easier as the material softens with humidity (Siau 1995). Treatments with glutaraldehyde caused a reduction in moisture content as WPG of wood increased during the sorption process (Figure 2b, c, and d). Compared to the EMC (21.6% at RH 95%) of untreated sample (Figure 2a), wood treated to WPGs of 0.5, 8.6, and 20.9% obtained the moisture content of 20.3, 15.3, and 11.3% (Figure 2b, c, and d), respectively. This shows that a considerable reduction in moisture adsorption occurs due to glutaraldehyde treatment. The total running time taken throughout the sorption run was apparently reduced by glutaraldehyde treatment of the wood and it reduced with increasing WPG (Figure 2). However, it has to be considered that the running time is related not only to the material properties but also to the sample mass and geometry used for DVS measurement. In this study, the mass and geometry of wood powder used can be assumed to be comparable and the total running time can thus reflect the sorption characteristics. The reduction in total running time might be due to the reduced moisture content sorbed by the treated wood.

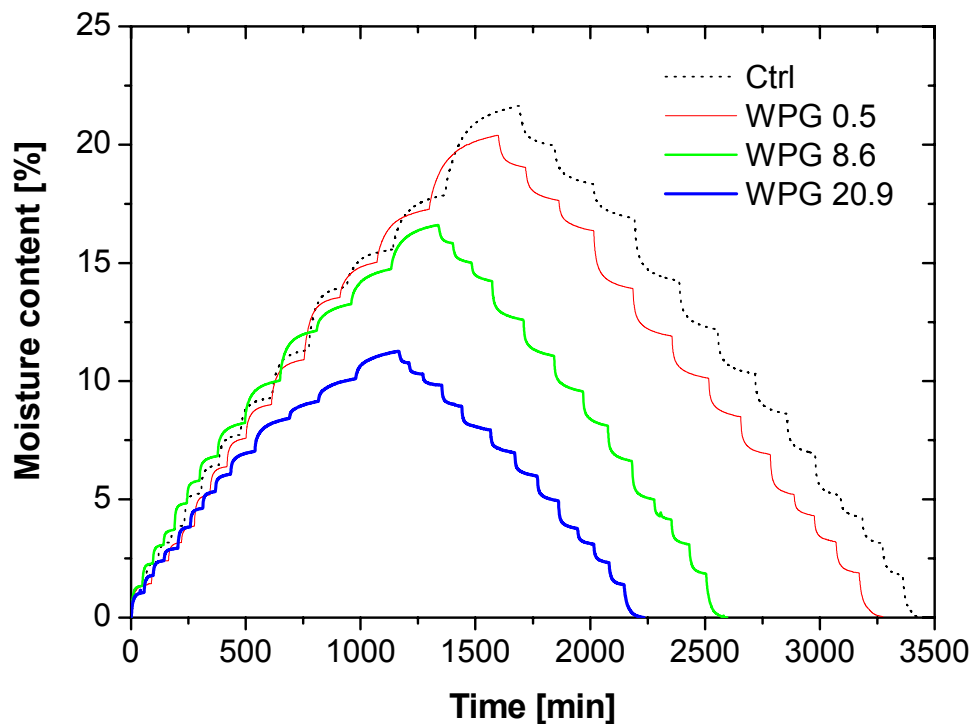


Figure 2: Moisture content of wood untreated and treated to WPGs of 0.5, 8.6, and 20.9% during the sorption run under stepwise target relative humidity.

Isotherm sorption of wood

In order to compare the effects of treatments on the sorption behaviour of wood, the adsorption and desorption isotherms of wood with different treatments were overlaid (Fig. 3a, b), respectively. The adsorptive curves of untreated and treated wood displayed a typical sigmoidal shape (Figure 3a) as were found in cellulose-based materials (Skaar 1988, Chatterjee *et al.* 1997). With the stepwise increase of RH, the moisture content of untreated wood increased (Figure 3a) due to the abundant hydroxyl groups and elastic swelling of cell walls by water. Treatment of wood to low WPG (0.5%) slightly reduced the MC in the high RH range of adsorption and desorption isotherms (Figure 3a and b).

Further increasing the WPG of modified wood caused an apparent reduction in EMC through both the adsorption (Figure 3a) and desorption (Figure 3b) run; the sigmoidal curves of desorption isotherms became linear (Figure 3b). This may be explained by the increased cell wall stiffness due to the microfibril crosslinking by glutaraldehyde. This reduction in moisture change (finally resulting in a low EMC of treated wood) due to modification may be explained by the physical and chemical interactions between glutaraldehyde and cell walls. As it has been well known, two aldehyde groups in the glutaraldehyde molecular chain may in principle react with four hydroxyl groups of wood thereby deactivating these water sorption sites. This will reduce the hydrate water adsorption in the low RH range. At the same time glutaraldehyde can crosslink the microfibrils resultantly restraining the swelling as the treated wood is exposed to humidity. In a moist environment diffusion of water into the crosslinked cell wall will essentially produce a compressive stress in the cell wall since it cannot swell as does the untreated one. Such a compressive stress can therefore result in the reduction of moisture adsorption (Skaar, 1988). Furthermore, incorporation of glutaraldehyde will locate in the nanopores of the cell wall and pre-swell the cell wall. As a result, the size (free space) of nanopores is reduced and the cell wall swelling due to water adsorption can also be diminished, which results in less accommodation for water (primary dissolved water and condensed water) in the high RH range (Hill 2008).

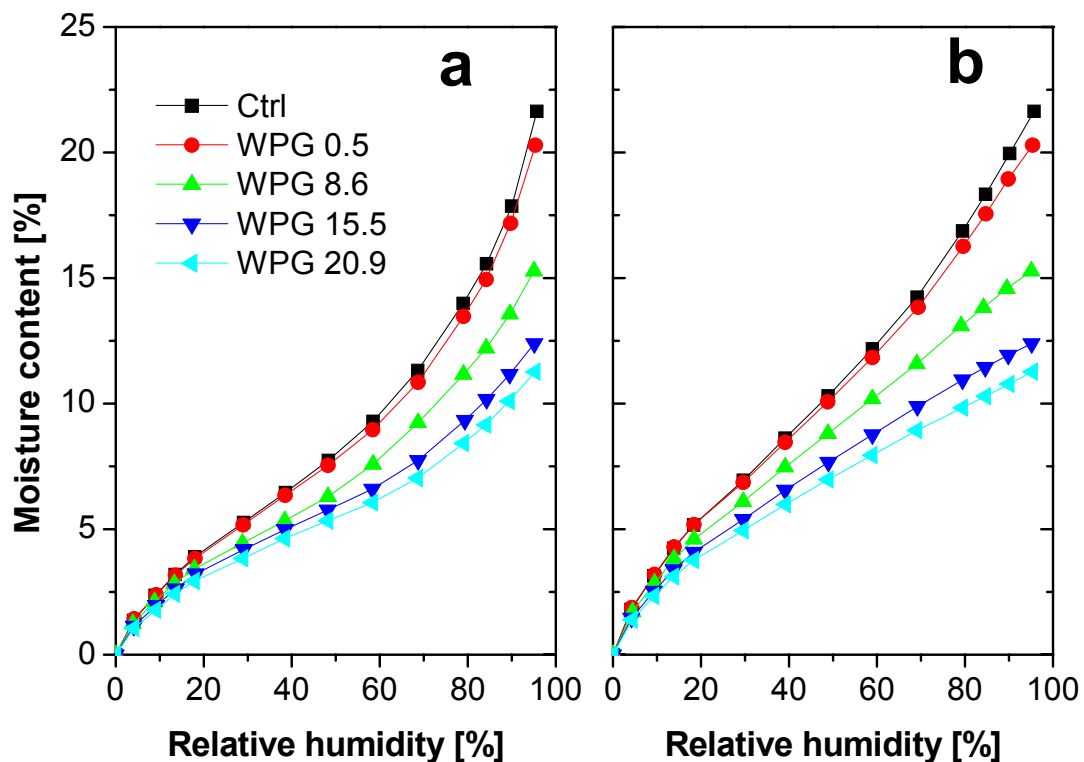


Figure 3: Moisture adsorption (a) and desorption (b) behavior of wood which is untreated or treated to WPG of 0.5, 8.6, 15.5, and 20.9%, respectively.

Sorption hysteresis of wood

With the same exposure history, modification of wood with glutaraldehyde also reduced the sorption hysteresis compared to untreated wood (Figure 4a). Wood treated to low WPG of 0.5% only displayed slightly less hysteresis at the RH of 85% and 90% compared to the untreated wood (Figure 4a). At the higher WPG levels, the sorption hysteresis of treated wood was reduced over the full hygroscopic range, especially in the high RH range, and the maximum hysteresis point shifted from 70% RH of untreated

wood to 60% RH for the modified wood (Figure 4a). A comparison of the loop areas of the isotherm sorption curve (referred to as total hysteresis) also evidenced that modification of wood with GA resulted in a reduction in the loop area up to 40% with the increase of WPG (Figure 4b). This further confirms the observation of a decrease in sorption hysteresis due to glutaraldehyde treatment (Figure 4a).

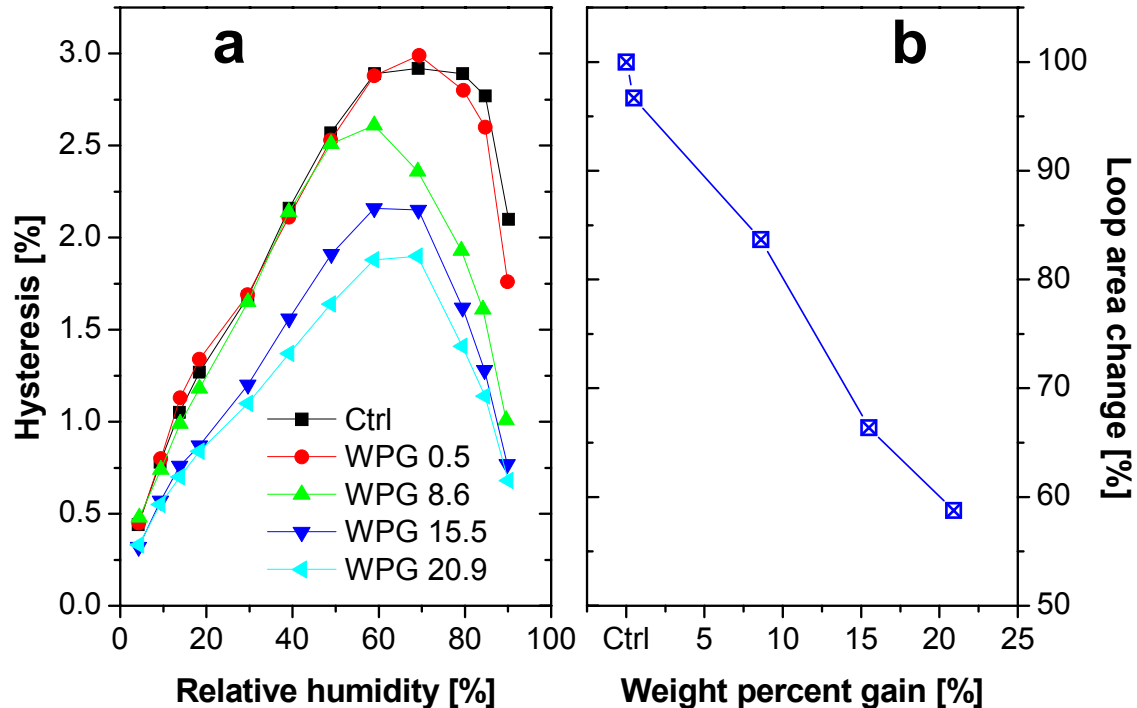


Figure 4: Hysteresis of untreated and modified wood during the sorption process (obtained by subtraction of equilibrium moisture contents between desorption and adsorption at the same target RH level (a) and the change of isotherm loop area of wood modified to different weight percent gain (on the basis of area of untreated wood) during the sorption process (The area was obtained by integrating the fitting curves of isotherm sorption data by four order polynomial fit, the $R^2 > 0.996$) (b).

Although the cellulosic materials present a higher moisture content at given RH in the desorption run than in the adsorption run thereby resulting in hysteresis, this does not mean that at a same given RH the moisture decrement of sample is always lower than its moisture increment previously obtained. A comparison of moisture increment and decrement at the same RH level through the sorption isotherm showed that in the RH range of 5 – 60%, the adsorption moisture increment was always lower than the desorption decrement (Figure 5). Over the RH of 60%, the increment was generally higher than the decrement at same given RH level, especially at the highest RH level of 95%. Modification of wood with glutaraldehyde distinctly reduced the difference between moisture increment and decrement (Figure 5b-d) compared to that of untreated wood (Figure 5a) in the isotherm run. The reduction of hysteresis of wood may be explained by the change of cell wall structure due to the chemical modification. The hysteresis effect has previously been interpreted on the basis of sorption phenomena on a glassy solid below the glass transition temperature (Hill et al. 2009a). At the adsorptive stage, the process of water molecules adsorbing onto the sorption sites of cell walls is an exothermic process. The thermal motion of incoming water molecules thus causes the expansion of cell wall nanopores thereby creating new internal surface. During desorption, relaxation of the cell wall matrices to the state it was in during adsorption is kinetically hindered (Lu and Pignatello 2002). Modification with

glutaraldehyde results in crosslinking and bulking of the cell walls due to the incorporation of chemicals (Yasuda and Minato 1994, Xiao *et al.* 2009). Crosslinking reduces the degree of freedom of cell wall polymers and the bulking pre-swells the cell wall. Both effects thus cause an increase of wood stiffness after treatment, which results in less deformation during the sorption process.

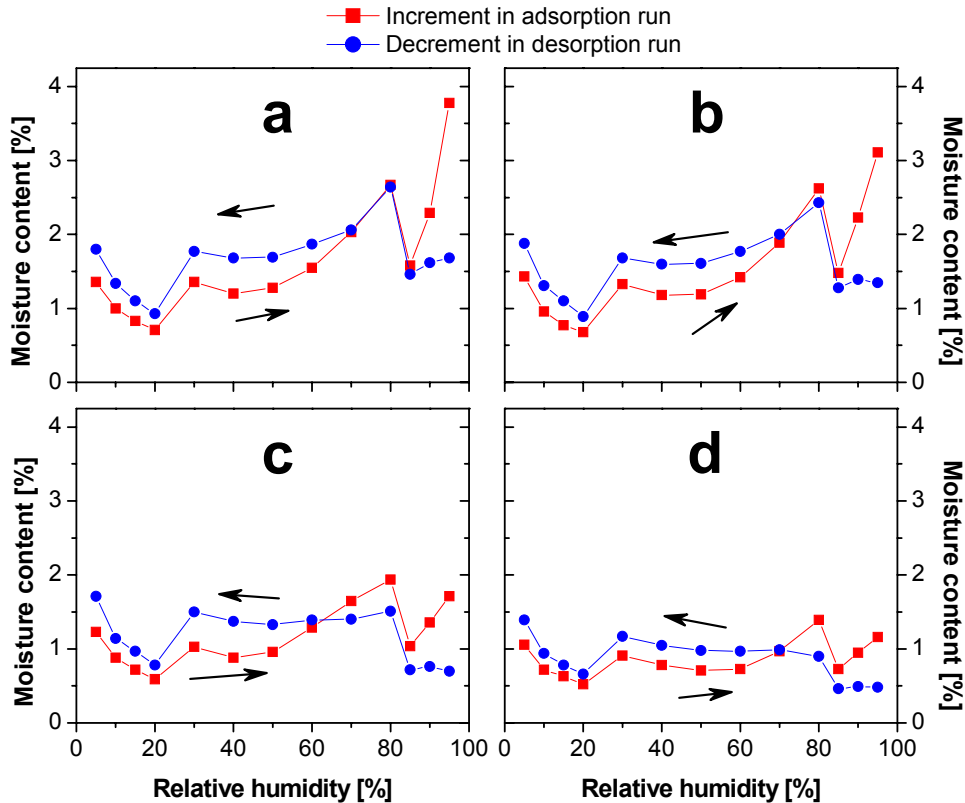


Figure 5: Moisture increment in the adsorption run (arrow direction, RH from 5% to 95%) or moisture decrement in the desorption run (arrow direction, RH from 95% to 5%) of untreated and treated wood at given RH levels. a: untreated control, b: treated to WPG of 0.5%, c: treated to WPG of 8.6%, d: treated to WPG of 20.9%.

CONCLUSIONS

Modification of Scots pine sapwood with glutaraldehyde to different WPGs caused a reduction in the EMC at different RH levels and total running time through the isotherm run. The sorption hysteresis exhibited between adsorption and desorption isotherms was reduced by glutaraldehyde modification, and this was more pronounced in the high relative humidity due to the reduction in the difference between adsorption moisture increment and desorption moisture decrement at the same relative humidity level. The desorption isotherm curve became more linear with increasing levels of modification. The modifying effects of glutaraldehyde on the sorption behaviour of wood may primarily be attributed to three aspects: (1) Reaction of aldehyde group with the hydroxyl groups of cell wall deactivates the sorption sites; (2) Crosslinking of cell wall microfibrils by glutaraldehyde reduces the elasticity of cell wall material and makes the cell wall stiffer; (3) Bulking due to incorporation of glutaraldehyde into cell wall pre-swells the cell wall and reduces the free space of nanopores in the cell wall.

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Wood Chemical Treatment Influence on the Physico-chemical Interaction of Phenolalcohols with Wood and Its Components

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Keywords: Wood, chemical treatment, wood components, phenol alcohols, diffusion, sorption

ABSTRACT

The purpose of the work was to investigate influence of acetylation, splitting of ester bonds in wood structure by ammonia vapour and hydrolytic treatment of birch wood on the penetration kinetics of phenol alcohols (PhA) in wood cell walls. Wood with lumens filled with paraffin in the part of experiments for this purpose was used. Besides that, sorption capacity of wood and its isolated components – cellulose, holocellulose and Bjorkman lignin towards model substance ortho-hydroxymethyl phenol (saligenin) was measured. It was shown that swelling kinetics of wood in the PhA solution can be described by second-order chemical reactions equation. Equilibrium swelling of acetylated wood in PhA was about 2 times higher than original wood. Swelling increase also at gradual elimination of hemicelluloses from wood. Treatment with ammonia and hydrothermal treatment at 140°C increased swelling predominantly in the direction of lumens. The experiments showed, that PhA concentration in the cell walls is lower than in the original solution. At investigation of sorption capacity of wood and its components towards saligenin it was found that cellulose sorption capacity is very low; for holocellulose – about 8 times higher. High sorption capacity was observed for the lignin preparation. Treatment of lignin with 5% HCl drastically diminish the sorption because the physical and chemical inactivation of the preparation. Wood sorption capacity was between that for the lignin and holocellulose. Treatment of wood with ammonia diminish the sorption capacity in all range of saligenin concentrations but acetylation at least 2 times increase. Dependence of sorption capacity on temperature allowed to calculate the differential heat of sorption of saligenin on wood – it was between 4,3 and 5,3 kJ/mol, depending on the sorbed quantity of the substance. At using wood dewatered by solvent-exchange technique and saligenin solution in low polar solvent – chloroform the sorption energy increase to 19-21 kJ/mol.

INTRODUCTION

Phenol-formaldehyde resins are often used for the production of different wood-based materials, in particular, plyboards, flake boards, moulded and pressed articles. The properties of these materials considerably depend on the location of resin in the wood structure and physical or chemical interaction with wood substance. So it is well known that form stability of the material considerably increase and water sorption capacity decrease at formation of polymer in the cell wall structure (Stamm 1964). Impact strength of the material at the same time decrease. From the other side properties of the obtained composites considerably can be changed by altering the wood structure by previous chemical treatment of wood. So, it can be expected, that at gradual elimination of more hydrophilic part of the wood – hemicelluloses by acid hydrolysis or

hydrothermal treatment the water stability of the material can be improved. The same effect can be reached at diminishing of hydroxyl group content in wood, for example, by acetylation. At splitting of intermolecular ester bonds between the wood components it was expected that the plasticity of the material at production of wood-filled plastics can be improved. Every treatment of wood change the diffusion process of resin in wood structure and physical or chemical interaction of the resin solution with wood substance. Task of this investigation was to elucidate the effect of elimination from wood hemicelluloses by hydrolysis with 5% HCl at different temperatures or hydrothermal treatment, splitting of ester bonds in cell walls by wood treatment with ammonia vapours and acetylation of wood on the diffusion kinetics of phenolalcohols solution, quantity of the resin in cell walls and sorption capacity of wood and its components towards one of the representative of PhA – o-hydroxymethyl phenol (saligenin).

EXPERIMENTAL

Birch wood specimens with dimensions 20x20x5 mm (T, R, L) extracted with ethanol-benzene mixture than then with hot water and dried till constant weight were used for the experiments. Part of the specimens before experiments were impregnated with molten paraffin at 95°C under vacuum. Calculated void filling degree 84-87% from the theoretical value. With ammonia vapour wood, containing 12-14% moisture, was treated at pressure 0.3 MPa during 20 h. The specimens after treatment and drying retained practically volume of the original wood. Wood was acetylated with acetic anhydride at 120°C for 20 h. Residual reagent was removed by washing of specimens with water with subsequent drying. Weight increase in the result of acetylation 21.31% volume increase 10,2%. For the elimination of hemicelluloses wood was treated with 5% HCl at 60-100°C. Specimens after treatment were washed with distilled water till neutral reaction and dried. For the sorption experiments wood sawdust with particle size 0.6-1,5 mm was used. Holocellulose was isolated by classical peracetic acid method, but lignin – according to Bjorkman's method (Bjorkman 1956, Bjorkman and Person 1957)

Phenol alcohols were synthesised at molar proportion of the components phenol/formaldehyde /sodium hydroxide 1/1.3/0.019 at temperature 65°C; heating time 7 h. The product dry residue after heating at 150°C was 52.5%, density 1.146 g/cm³; phenol content 7.1%; pH 9.0. O- and P-hydroxymethyl phenols were synthesised according to described in literature method (Brink 1965) by reduction of salicyl or p-oxibenzyl aldehyde with NaBH₄ in alkaline medium.

The swelling of wood was followed by clock – type micrometer with accuracy ±0.01 mm at temperature 22±10°C. The content of phenolalcohols in wood was determined by drying impregnated specimens at room temperature in vacuum under P₂O₅ for elimination of condensation processes. For the measuring of the PhA content in cell walls the same operation was repeated with specimens filled with paraffin. The concentration of PhA in wood was calculated comparing mass of specimens before and after drying. The diffusion coefficients for PhA penetration in wood were calculated according to described in literature method (Malkin and Chalych 1979) using paraffin-filled specimens. The sorption experiments were performed at using 0.1-0.4 M solutions of phenolalcohols at wood/liquid proportion 1:10; sorption time – 24 h. The concentration of phenolalcohols in solution was determined at using the bromide-bromate method

RESULTS AND DISCUSSION

As already mentioned above the aim of the investigation was to elucidate chemical treatment (gradual elimination of hemicelluloses by acid hydrolysis, splitting of ester bonds by treatment with ammonia and acetylation) effect on the penetration of low-molecular phenol-formaldehyde condensation products in wood structure. HCl hydrolysis influence on the wood weight loss and volume changes were reflected in Table 1. The weight loss is almost proportion to hydrolysis temperature and at 100°C practically all HC (residual HC 3%) were eliminated with simultaneous shrinking of specimens volume.

Table 1: Results of wood hydrolysis with 5% HCl

Changes	Temperature [°C]					
	50	60	70	80	90	100
Weight loss[%]	2.8	4.8	12.0	18.1	26.2	33.2
Volume loss [%]	2.4	4.4	8.4	12.0	18.1	19.6

Hydrothermic treatment at temperatures till 140°C substantially did not change the weight and volume of specimens (changes 2.9% and 1.6% correspondingly). The same was observed for wood treated with ammonia vapour. Acetylated wood had weight increase 21,3% and volume increase 10,2%. Swelling curves of wood in water (Figure 1) and in PhA solution (Figure 2) demonstrated that in water the equilibrium was reached during 1-3h, but in PhA solution 2-4days considering different dimensions of molecules.

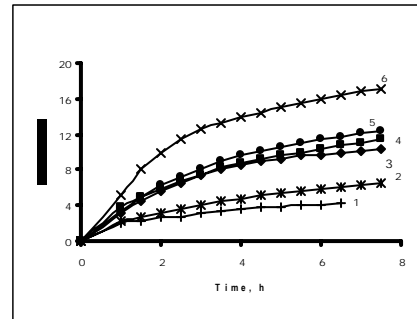
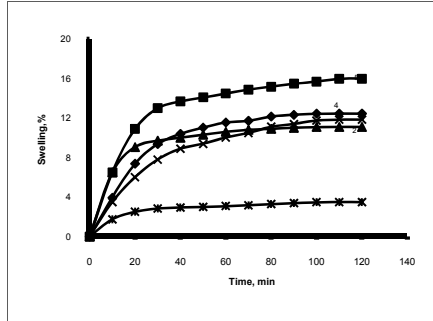


Figure 2: Chemically treated wood swelling in water; 1 – acetylated wood; 2 – HCl 100°C; 3- in PhA solution: 1 – acetylated wood; 2 – wa-NH₃- treated wood; 4 – untreated wood; 5 – ter 140°C; 3 – untreated wood; 4- HCl 60°C; HCl – 60°C. 5 – NH₃- treated; 6 – HCl 100°C.

As expected, the lowest swelling was observed for the acetylated wood. In all cases swelling of wood in PhA solution exceeded that of water, especially for the acetylated wood as a result of increasing of organophylic properties of the wood substance after acetylation.

For the comparison of swelling rates of wood in water and PhA solution we tried to apply other authors (Schwabe and Phillips 1954) observation that for penetration kinetics description some chemical reactions kinetics equations are valid. In our case swelling process in PhA for comparatively long period obeyed second order chemical reaction equation $da/d\tau = k_2(a_\infty - a_\tau)^2$ or $k_2\tau = a_\tau/a_\infty(a_\infty - a_\tau)$ where $da/d\tau$ - dimensions change in time unit and a_∞ - swelling at equilibrium and k_2 –swelling rate constant (Figure 3.)

Table 2: Equilibrium swelling of chemically treated wood in water and PhA solution.

№	Treatment	Equilibrium swelling, [%]	
		In water	In PhA solution
1	Untreated wood	12.5	15.1
2	5% HCl, 60 ⁰ C (weight loss-5,2%)	16.0	18.3
3	5% HCl, 100 ⁰ C(weight loss 33%)	11.1	14.2
4	Water 140 ⁰ C(weight loss 2,2%)	12.3	12.4
5	Ammonia vapour	11.8	15.9
6	Acetylation	3.5	8.0

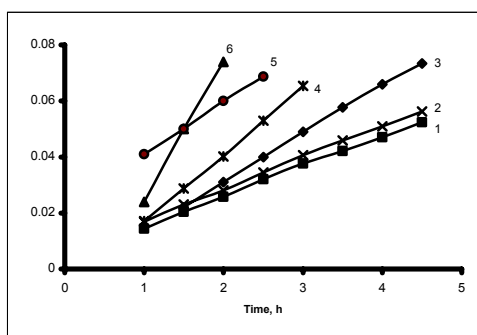


Figure 3: Isotherms of wood swelling in PhA solution in coordinates of second order chemical reactions coordinates :1- HCl 60⁰C;2- hydrothermal treatment 140⁰C;3- untreated wood;4-NH₃ treated; 5 –acetylated wood; 6 – HCl 100⁰C. (Y-axis denotation $a_t/a_\infty(a_\infty-a_\infty) \cdot 10^{-2}, [\%]^{-1}$).

Calculated swelling rates for different treated wood samples at $a_t/a_\infty = 1/3$ in PhA solution and in water demonstrated (Table 3) that wood swelling in water is approximately 10 times faster than in PhA solution. HCl hydrolysis at increasing of treatment temperature at first diminish the wood swelling rate in PhA solution and at temperature 100⁰C (when practically all hemicelluloses are removed and wood structure partly destroyed) – sharply increase. Treatment with water at 140⁰C somewhat decrease swelling rate.

Table 3: Swelling rates of chemically treated wood in water and PhA solution.

Wood treatment	Swelling rates [%/min]	
	In water	In PhA solution
Untreated wood	0.33	0.029
HCl 60 ⁰	0.69	0.028
HCl 80 ⁰ C	-	0.019
HCl 90 ⁰ C	-	0.027
HCl 100 ⁰ C	0.60	0.119
Water 140 ⁰	-	0.013
NH ₃	0.28	0.049
Acetylation	0.14	0.0083

NH₃ treatment increase swelling rate but acetylation considerably decrease. In these experiments water and PhA solution penetrate in wood simultaneously in lumens and in cell walls. For the evaluation of penetration kinetics of PhA solution in cell walls the wood specimens with lumens filled with paraffin were used. Such approach for the determination of diffusions coefficients, although with some objections, considering that it is impossible to fill all theoretically calculated void volumes in wood, was used in

investigations of some other authors (Stamm 1954, Yokota 1962) For the calculation of diffusion coefficient equation $D = 0.04939 (\tau_{0.5}/l^2)$ was used where $\tau_{0.5}$ – time for half swelling of specimens; l – thickness of the specimens in the direction of diffusion. At calculating in such way diffusion coefficient for water in original wood specimens value $2.5 \times 10^{-7} \text{ cm}^2/\text{s}$ was obtained which is comparatively close to value obtained by other authors (Stamm 1954) at using wood specimens with voids filled with metal – $4.6 \times 10^{-7} \text{ cm}^2/\text{s}$. Calculated diffusion coefficients for PhA solution in differently treated wood (Figure 4.) demonstrated that these are considerably lower than for water (for untreated wood 8.4×10^{-8} ; for NH_3 – treated 6.7×10^{-8} ; for water treated at 140°C ($6.2 \times 10^{-8} \text{ cm}^2/\text{s}$) The lowest value – 2.3×10^{-8} was found for acetylated wood.

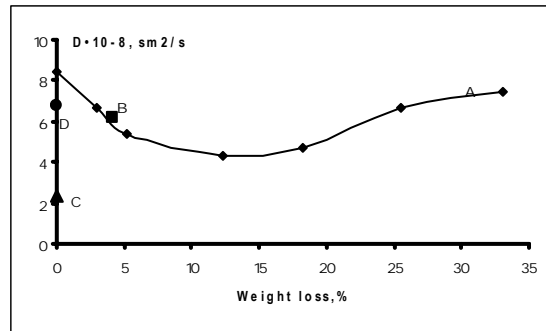


Figure 4: Effect of hydrolysis of wood with 5% HCl [A]; hydrothermal treatment at 140°C [B]; acetylation [C] and NH_3 treatment [D] on the value of diffusion coefficients for PhA solution penetration in wood cell walls.

Gradual elimination of hemicelluloses from wood induce formation of more dense structure of cell walls and diminishing of diffusion coefficient till weight loses about 15 %. Further, considering destruction of cell walls, diffusion rate increase. Comparing of paraffin-filled samples weight before and after drying in vacuum till constant weight allow to calculate PhA concentration in cell walls (Figure 5) Initial PhA concentration in solution at drying in vacuum was $55 \pm 1\%$. At first time, because of selective diffusion of water, the PhA concentration in cell walls is considerably lower than in original solution (excepting the first moment when PhA are sorbed by outer surface of wood) Further the concentration gradually increase but allways it was for about 4-5% lower than in original PhA solution. At comparing PhA solution concentration in cell walls of chemically treated wood (Table 4.) at equilibrium, it is evident that destruction of wood structure ($\text{HCl } 100^\circ\text{C}$) leads to increasing of the concentration

In acetylated wood cell walls the PhA concentration is higher than in original solution considering organophylic properties of the material and the lower density of hydrogen bonds. In cell walls the PhA are sorbed by wood components. Using as models isolated wood constituents – cellulose, holocellulose and lignin and saligenin as PhA model, sorbtion capacity of the components at different saligenin concentrations was determined (Figure 6). As was found by other authors (Sato 1964) the cellulose sorbed very low amount of phenolalcohols (curve 1) For holocellulose sorption capacity is considerably higher (curve 2); High amounts of saligenin were sorbed by lignin (curve 5) because of structure similarity. Wood sorption capacity is intermediate between for holocellulose and lignin and a bit higher than calculated from constituent sorption (curve 3).

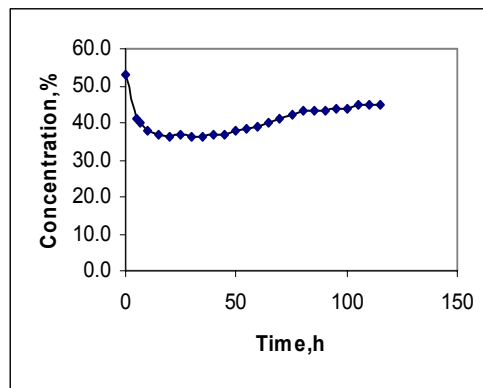


Figure 5: PhA concentration in the cell walls change at storing paraffin-filled Original wood specimens in PhA solution

Table 3: Concentration of PhA solution in cell walls at equilibrium.

Wood treatment	PhA concentration [%]
Untreated wood	46
Water 140 ⁰ C	44
NH ₃ treated	49
HCl 60 ⁰ C	44
HCl 100 ⁰ C	55
Acetylated wood	61

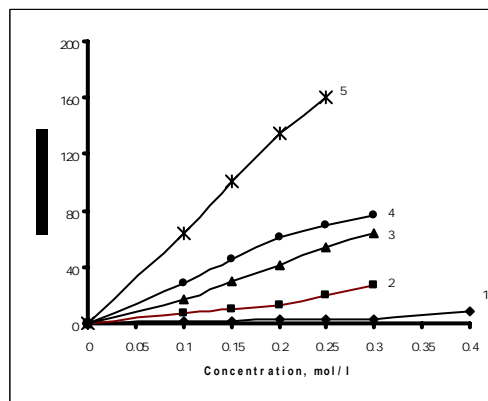


Figure 6. Saligenin sorption by birch cellulose [1]; holocellulose [2]; wood [4]; and lignin [5]; 3 – wood sorption isotherm calculated from the sorption capacity of components.

Treatment of wood with 5% HCl at 60⁰C diminish sorption but at higher temperatures - lightly increase. Treatment in the same way of isolated lignin considerably diminish its sorption capacity because chemical and physical inactivation of the preparation. Acetylation several times increase the wood sorption capacity regarding saligenin but NH₃ treatment substantially did not it change. At measuring of saligenin sorption by wood at 3 different temperatures (1.5;32 and 60⁰C) isosteric sorption energy was calculated : 4.1-5.7 kJ/mol. With increasing saligenin concentration the energy decrease. This value include desorption energy of water molecules from wood hydroxyl groups, desorption of water molecules from saligenin and interaction energy of saligenin with wood substance. That is why at using in our experiments as solvent chloroform and wood dewatered by means of solvent exchange technique the sorption is considerably higher - till 200 mg/g and sorption energy 19-21 kJ/mol. In our experiments at

comparing o- and p-hydroxymethylphenol sorption by wood it was found that the second was sorbed in lesser extent than the first.

CONCLUSIONS

At impregnation of wood with phenolalcohol solutions the swelling equilibrium is reached in almost 10 times longer period than in water. At first period water molecules are selectively sorbed by cell walls and that leads to considerably lower PhA solution concentration in cell walls than in the original solution. At further storing of wood specimens PhA solution concentration in cell walls gradually increase. Wood swelling process in PhA solution can be described by second-order chemical reactions equation and swelling rates can be compared. Gradual elimination of hemicelluloses from wood at first induce diminishing of swelling rate and then an increase because of destroying of wood structure. Wood treatment with NH_3 increase swelling rate but acetylation - decrease. At the same time acetylated wood in PhA solution at equilibrium swells about twice of that in water. At investigation of sorption capacity of wood and wood components – cellulose, lignin and holocellulose towards model compound o-benzylalcohol (saligenin) it was demonstrated that cellulose sorption capacity is very low but for lignin - high. Wood swelling capacity is that of between holocellulose and lignin. Differential sorption energy of saligenin to wood was found to be 4.1-5.7 kJ/mol.

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Session Three: Thermal modification

Hydrothermal Modification of Soft Deciduous Wood: Bending Strength Properties

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Keywords: Alder, aspen, bending strength, birch, chemical composition, hydrothermal modification

ABSTRACT

In comparison with the case of coniferous and hard deciduous wood, the thermal modification of soft deciduous wood has not been adequately studied, and its volumes of trade are relatively negligible. However, tendencies and aspirations are observed to use the wood of this local fast-growing species in construction more extensively. The thermal modification of aspen, grey alder and birch wood could open up wider possibilities for use under elevated moisture conditions, both indoors and outdoors. The aim of the study was to elucidate, how the changes in the mass, density and chemical composition of wood, hydrothermally modified at different parameters, influence the statistic bending strength properties of the material. For alder wood, in contrast to aspen and birch, the greater changes of bending strength are at the regime 160°C/1 h, but, intensifying the treatment, the decrease in strength is gradual. At lower modification temperatures, the bending strength of aspen and especially birch grows, in comparison with the case of untreated wood. The bending strength essentially decreases at the treatment 160°C/3 h, and decreases dramatically at the modification regime 180°C/1 h: in this case, this decrease does not depend directly on the material's mass losses and the decrease in density. As a result of hydrothermal modification (HTM), hemicelluloses degrade, and the relative amounts of cellulose and lignin increase. The composition of the chemical components of alder wood is more thermally stable, probably due to the higher content of lignin. In its turn, the thermal degradation of birch hemicelluloses is most pronounced. No correlation was found between the changes in the content of individual chemical components and the decrease in bending strength. Further studies in this direction on the effect of the hemicelluloses composition, degree of polymerisation of cellulose as well as lignin changes on the properties of hydrothermally modified soft deciduous wood are required.

INTRODUCTION

The object of the present study is soft deciduous wood, and its choice is determined by the availability of this material in Latvia, its uniform use, and the manufacturers' interest in obtaining high-value products from local resources in the forest field, which is very important for Latvia. In Latvia, soft deciduous trees comprise almost 48% of the total growing stock, which is almost 300 million m³. From this volume, 28% is birch, 8% is aspen, and 15% - grey and black alder. We have found in our studies that, by way of hydrothermal modification (HTM) at relatively low temperatures, it is possible to improve the biological durability of these soft deciduous trees' wood, to decrease the

moisture adsorption and increase the surface hydrophobicity (Andersons *et al.* 2010). It has been found that, in the same hydrothermal modification conditions, modified aspen, birch and grey alder wood with different resistance against rot fungi is obtained, and the bending strength changes also have a different character. The aim of the work was to establish the relationship between the bending strength changes of the hydrothermally modified wood of the tree species under study in relation to mass losses, wood density and chemical composition.

EXPERIMENTAL

For modification, birch (*Betula* spp.), grey alder (*Alnus incana*) and aspen (*Populus tremula*) wood boards without any visible defects were chosen. Moisture content before the treatment was 6-8%; for modified wood after the treatment, it was within a range of 3.5-5.5%, and after conditioning 5-6%. The initial wood average densities (at W 12%) were 546 kg/m³, 524 kg/m³ and 719 kg/m³ for grey alder, aspen and birch, respectively. The boards' average sizes were: length 1000 mm, width 75 mm, and thickness 25-32 mm for aspen and grey alder; length 970 mm, width 99 mm, and thickness 12 mm for birch. Hydrothermal modification was carried out in a WTT experimental laboratory device in a water vapour medium at temperatures of 140-180°C for 1 h or 3 h under elevated pressure (5-9 bar) conditions. Mass loss and wood density changes prior to and after modification were determined (measurements for 12-15 samples for each variant). Bending properties of birch wood were determined according to the EN 310 standard. Bending strength of aspen and grey alder wood samples was determined according to the DIN 52186 requirements. Before testing, the samples were conditioned according to the DIN 50014 requirements (air temperature 20 ± 2°C, moisture 65 ± 3%). 20 samples from each treatment and different boards were taken for the tests. Changes in the chemical component composition of modified wood (extractives, cellulose, lignin) were analysed (Zakis 1994). Extractives were determined, extracting the wood with acetone for 6-8 h in a Soxhlet extractor. Cellulose was determined by the Kirschner-Hoffer method, acting upon the wood with a mixture of concentrated nitrous acid and ethanol. The Klason lignin content was determined in compliance with the ASTM method D 1106-96, hydrolysing the wood chips with 72% sulphuric acid, and then performing the full hydrolysis of the oligosaccharides with 3% sulphuric acid at 100°C. Hemicelluloses were determined indirectly - as a difference between 100% and the analytically determined cellulose and lignin sum in acetone extracted wood.

RESULTS AND DISCUSSION

The decrease in the wood strength properties as a result of the thermal action is caused by the mass and density losses, connected with the chemical components' degradation and the changes in the cell wall structure.

Changes in the bending strength of HTM wood in relation to mass and density losses

Mass losses for aspen, birch and alder wood *versus* the treatment temperature are shown in Figure 1.

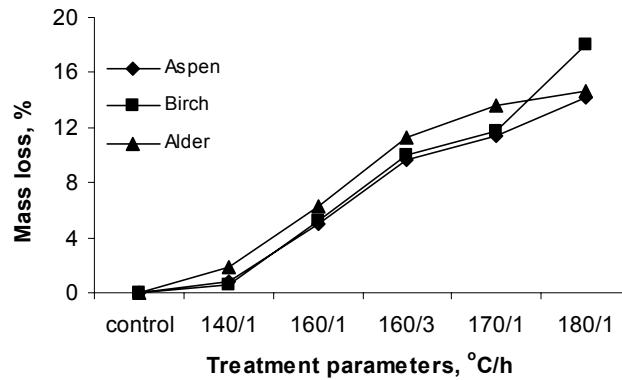


Figure 1: Mass loss of HTM wood versus treatment temperature

In the modification temperature range 140-170°C, mass losses grow gradually, and there is no essential difference among all the wood species under study (differences in the range 1-2%). With increasing temperature from 170°C to 180°C, alder mass losses grow only by 1%, respectively, the chemical composition of the matrix becomes relatively thermally stable; in contrast, aspen and especially birch wood components continue to degrade thermally, and mass losses grow by 3.2% and 6.2%, respectively. As a result of the modification for 1 h in the temperature range 140-180°C, birch wood mass losses grow linearly. Figure 2 shows relationships between the wood density and mass losses.

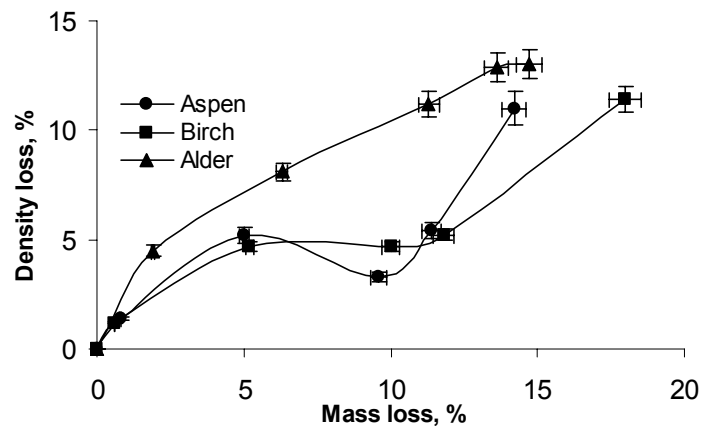


Figure 2: Relationship between density and mass losses for HTM wood

Alder wood density decreases linearly, with the increase in mass losses, in the temperature range 140-170°C; hence, the samples' volume changes proportionally to the mass losses. The decrease in mass losses by ~1% at 180°C for modified wood does not change the wood density. In the temperature range 160-170°C, densities for modified aspen and birch wood are the same, despite the increased mass losses, obviously owing to the greater decrease in the samples' sizes (respectively, volume). With increasing temperature from 170°C to 180°C, the percentage decrease in density for aspen and birch is the same, despite the different mass losses, which is explained by a higher initial birch wood density, in comparison with the case of aspen (524 kg/m³ and 719 kg/m³, respectively). With increasing treatment intensity, the statistical bending strength of wood decreases (Figure 3).

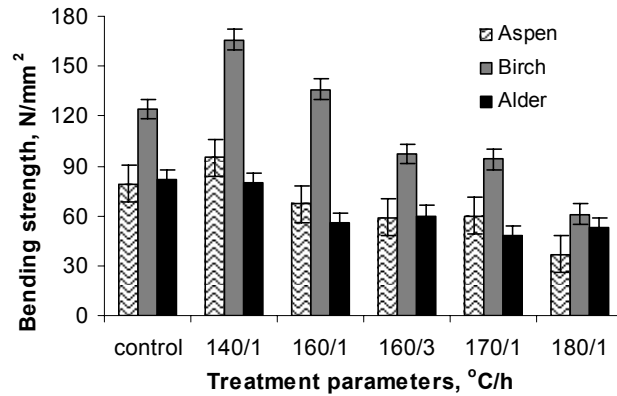


Figure 3: Static bending strength properties of HTM wood

Bending strength for unmodified aspen and alder wood is similar. Modifying at the regime 160°C/1 h, bending strength for alder wood, in comparison with the case of aspen and birch wood, decreases most intensively (by ~30%), but changes comparatively little at more intensive regimes, despite the increased mass losses and the decrease in density. In the case of the modification regime 140°C/1 h, bending strength for aspen is higher than that for unmodified wood; at more intensive treatment, it decreases and changes little in the temperature range 160-170°C. Kocaefe and co-authors (Kocaefe *et al.* 2007) have found that, for aspen wood at the temperature about 160°C, exothermal reactions related structural changes occur, which refer to the wood hardness properties. For HTM birch wood, bending strength increases, modifying at 140 °C/1 h and 160 °C/1 h, but decreases linearly at the treatment regimes 170 °C/1 h and 180 °C/1 h. The HTM regime at 180 °C/1 h results in the following bending strength loss: 53.2%, 50.8%, 35.4% for aspen, birch and alder, respectively. Johansson (Johansson 2008) has found a lower decrease in bending losses for birch wood, modified at 200°C for 3 h, namely, by 43%. The author also has found no indications of the increase of strength in birch wood, thermally treated at temperatures between 175°C and 200°C, which agrees with the data obtained by us. On the contrary, Shi (Shi *et al.* 2007) has indicated a minor growth in bending strength for birch in the case of the modification by the ThermoWood method at the temperature up to 200°C. The relationship between mass, density and bending strength losses for aspen, birch and alder is shown in Figures 4-6, respectively. The density of aspen wood decreases comparatively evenly, with increasing mass losses according to the increase in the treatment intensity (Figure 4). These changes do not explain the dramatic decrease in bending strength at the regime 180°C/1 h for modified wood. The same can be applied also to the HTM birch wood (Figure 5). For alder, after the more dramatic decrease in bending strength for the wood, modified at the regime 160°C/1 h, the further changes, with increasing mass and density losses according to the treatment intensity, are not so pronounced.

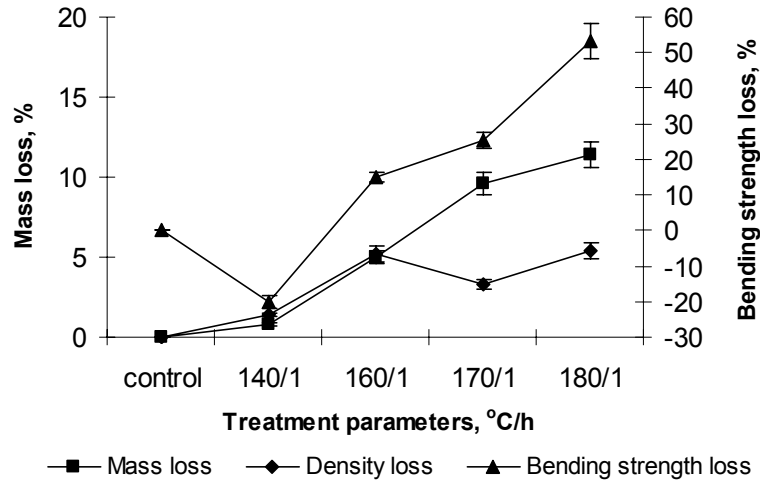


Figure 4: Relationship between mass, density and bending strength losses for aspen wood

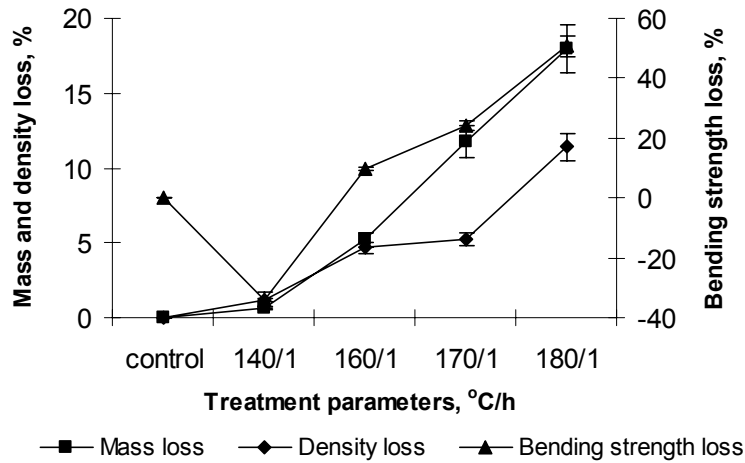


Figure 5: Relationship between mass, density and bending strength losses for birch wood

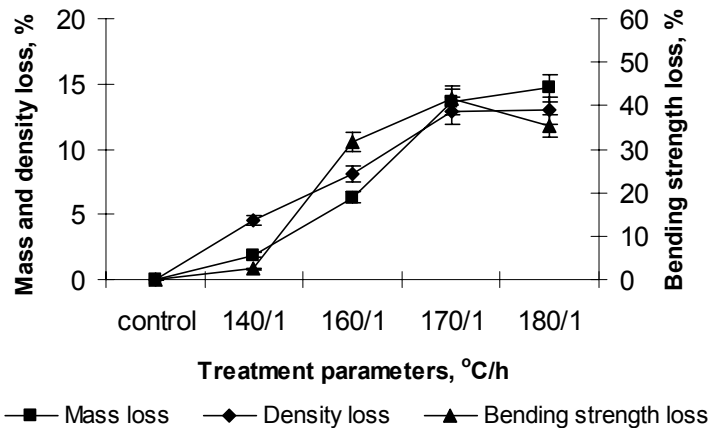


Figure 6: Relationship between mass, density and bending strength losses for alder wood

Bending strength loss and chemical composition changes of modified wood

It can be seen that the bending strength losses by ~35% for aspen and birch wood, at the treatment regime 180°C / 1 h, are not explained by at the same time comparatively minor

percentage mass (3 and 6%, respectively) and density (~5%) losses at 170°C/1 h. Therefore, a relationship with the degradation of individual chemical components was looked for. The bending properties of thermally modified wood, as well as those of unmodified wood, are determined by the cell walls' chemical and structural composition, even up to the molecular level (Arnold 2010). Our results testify that, for all the woods under study, the degradation of hemicelluloses is the easiest and highest; as a result, the relative amounts of cellulose and lignin grow, and the whole matrix structure changes. For the investigated wood, a dramatic degradation occurs beginning with the temperature 160°C (Figure 7).

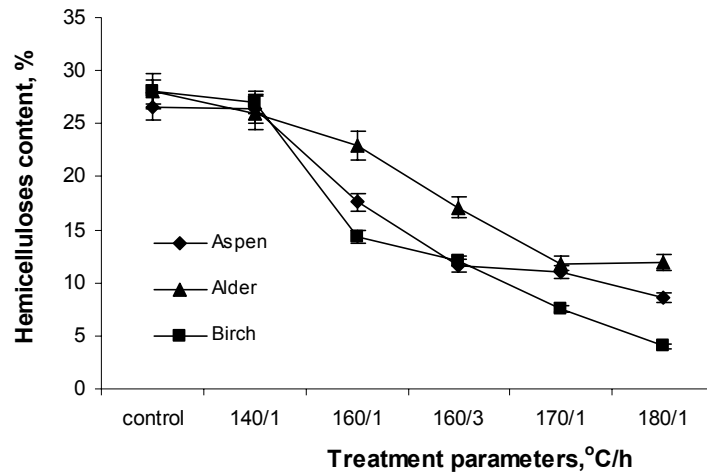


Figure 7: Changes of hemicelluloses in HTM wood

At more intensive regimes, the hemicelluloses changes are different. For alder, the maximum amounts of hemicelluloses are degraded at 170°C/1 h, and the losses are negligible at 180°C. For aspen and birch, the hemicelluloses content, with increasing temperature, continues to decrease gradually. The birch wood, modified at the regime 180°C/1 h, has only 4% of hemicelluloses; 8.6% and 11.9% of hemicelluloses remain in aspen and alder wood, respectively. The hemicelluloses content changes in HTM aspen and birch do not explain either the growth in bending strength at lower treatment temperatures, or the dramatic decrease in strength at the regime 180°C/1 h (Figure 8).

Hardwoods are less thermally stable than softwoods. The reason for the lower stability of hardwood hemicelluloses is the higher percentage of pentosans, which have a more reactive structure than hexosans. According to Fengel and Wegener 1989, the pentosan content in soft deciduous wood is as follows: 23.0% for alder (*Alnus glutinosa*), 17.2% for aspen (*Populus tremuloides*), and 25.3% for birch (*Betula verrucosa*). It should be mentioned that the amounts of hemicelluloses, indicated in different publications, are different. Probably, the higher xylose content in birch wood is the reason for the lower thermal stability of hemicelluloses. In the case of alder, probably, the higher content of lignin in the lignocarbohydrate complex protects hemicelluloses from thermal degradation.

We also did not find any direct relationship between the growth in the relative amounts of cellulose and lignin in modified wood and the statistic bending strength changes. One of the reasons for the dramatic decrease in bending strength at 180°C could be the changes in the cellulose structure. However, according to Fengel and Wegener (1984), the degree of polymerization is already decreased at temperatures above 120°C. Sundquist and colleagues (Sungquist *et al.* 2006) have shown that the thermal treatment

of birch wood under acidic pH conditions in the temperature range 160-200° causes the decrease in the cellulose average molecular size and concluded that this fact has a crucial effect on the observed decrease of mechanical strength in thermally treated wood.

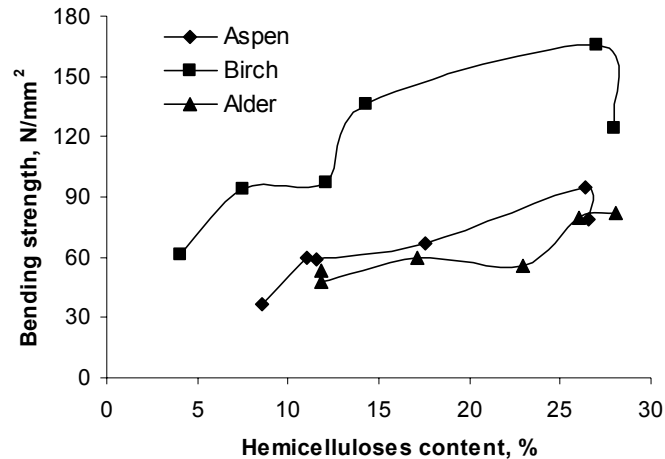


Figure 8: Bending strength loss in relation to the hemicelluloses content

Our TGA data testify a lower thermal stability of cellulose for aspen wood, modified at the regime 180°C/1 h, in comparison with the case of aspen wood, modified at 170°C/1 h. Probably the reason for this is the decrease in the degree of polymerisation of cellulose as a result of the hydrothermal action. This is not found for HTM birch cellulose. TGA spectra also testify a lower stability of HTM aspen and birch lignin at the treatment 180°C/1 h. The bending strength of wood could be decreased also by the lignin condensation, as a result of which the polymer material's elasticity decreases. To understand the mechanical properties in relation to the changes in the chemical composition and structure, further investigation is required.

CONCLUSIONS

As a result of HTM, with increasing treatment intensity in the temperature range 140-180°C, mass losses for birch wood increase linearly, reaching 18%. With increasing modification temperature from 170 to 180°C, the degradation of aspen wood slows down, but alder wood becomes thermally stable, i.e. mass losses are ~1%. The decrease in the alder wood density under the thermal action testifies the wood volume changes proportionally to mass losses; on the contrary, for aspen and birch wood at the temperature 160-170°C, the sizes decrease essentially. The statistic bending strength of alder decreases dramatically at the regime 160°C/1 h for modified wood. Aspen is characterised by an increase in bending strength for wood, modified at 140°C/1 h, but birch – for wood, modified as well at 160°C/1 h; both woods are characterised by the dramatic decrease in bending strength, when modifying at the regime 180°C/1 h. As a result of the HTM treatment, hemicelluloses degrade, and the relative amounts of cellulose and lignin grow. Alder wood is more stable, but birch hemicelluloses are the most sensitive ones against the thermal action. No direct relationship has been found between the changes in aspen and birch mass, density and chemical composition, and the considerable decrease in bending strength at the HTM regime 180°C/1 h.

ACKNOWLEDGEMENTS

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High Quality Thermal Treatment Using Vacuum Based Technology to Come to More Homogeneous Durability

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ABSTRACT

The SmartHeat® thermal timber treatment is a new technology based on the process parameters being steered very precisely mainly due to the vacuum applied and heating system involved. Timber treated with this technology shows a potential for more homogeneous durability in one batch. Several batch treatments were sampled and assessed on statistical variability of decay resistance against Basidiomycetes and soft rotting micro-fungi according to lab testing as described in the standards CEN/TS 15083 part 1 and 2 respectively. By means of Weibull distribution assessment it was possible to show that variability in biological durability of each treated beam is well controlled and that this variability is limited compared to natural durability of wood species. Lower treatment variability due to precise parameter control for each beam and limited deviations of process parameters within the treating vessel are considered the main contributing factors. The paper also states that lower control of process parameters of some heat treatment processes might induce higher variability of the obtained biological durability than a customer might expect.

INTRODUCTION

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).

The need for a better quality control system was further underpinned by Welzbacher and Rapp (2002). They showed that protection against decay of wood that had been thermally modified by one of the four European commercial processes (Plato, ThermoWood, Retified wood or oil heat-treated wood) decreased in the order *Coniophora puteana* > *Coriolus 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.

Based upon the need to control the heating of each individual plank the Dutch company Lignius developed the SmartHeat® process. This is a heat treatment process under vacuum that allows mass control during treatment. This paper is presenting more details on the advantage of this process for fit-for-purpose production of material with a homogeneous biological durability.

Cartwright and Findlay (1946) defined durability as the ability of a material or object to endure. The durability of timber includes, therefore, its resistance to fungal decay, to insect attack, to mechanical wear and to the destructive effects of exposure to all types of weather such as frost, sunshine, sandstorms, etc. The term biological durability can be used to identify the durability of wood and wood products determined by decaying organisms like fungi and insects. Natural durability is in many cases referred to as the intrinsic durability of a wood species or wood assortment. Wood preservation which concerns a treatment and enables to identify a dose response of active ingredients used to prevent or eradicate activity of decaying organisms like fungi and insects can be defined as enhanced, conferred or induced durability. Although thermal modification is not based on an active ingredient dose response the enhanced durability can be evaluated similarly. There is no specific reason to assess the performance of wood and wood products with regard to service life prediction of a commodity or building component differently whether durability is intrinsic or conferred. Hence it is useful to elaborate on the overall biological durability approach to assess wood product performance in view of service life prediction (Van Acker and Stevens 2000).

This paper makes reference to work on improved statistical approach of biological durability of wood related to outdoor uses in out of ground contact situations (Van Acker *et al.* 2010). Starting with Weibull 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 only on fungal attack by Basidiomycetes. The option to work on a natural durability approach based on laboratory testing was earlier discussed (Van Acker *et al.* 1996). In this respect the European standard CEN/TS 15083-1 was developed to provide input for the overall natural durability standard EN 350. This methodology is based on earlier reported research by Van Acker *et al.* (1998, 1999 a, b).

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.

Findlay (1985) summarized that it is usual to classify timber into five classes in respect to their durability (Table 1). In his table reproduced below the corresponding 'life' of a

2 x 2 inch stake, in average soil, is compared with the average loss in dry weight per cent suffered in laboratory tests.

Table 1: Classes of natural durability of wood to fungal attack as defined by Findlay (1985)

Durability class	Life of test stake in the field, temperate, England	Life of test stake in the field, tropics, Fiji	Average loss in dry weight (%)
Very durable	Over 25 yr	Over 10 yr	Nil or negligible
Durable	15-20 yr	5-10 yr	Up to 5 %
Moderately durable	10-15 yr	(not given)	5-10 %
Non-durable	5-10 yr	2-5 yr	10-30 %
Perishable	Less than 5 yr	Less than 2 yr	Over 30%

Use class 4 (UC4) is defined as the condition of continuous soil or freshwater contact while UC3 is for outdoor uses 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. Therefore when focussing on applications related to UC3 it is not relevant to use results from ground contact service life testing. Hence natural durability classes as defined in EN 350 part 2 are not fully transferable to UC3 applications. Furthermore under UC3 a wide range of exposure conditions can be distinguished mainly different related to time of wetness induced.

A lot of valuable wood species are mainly used for use class 3 applications like window joinery, cladding, decking and garden furniture and it is of interest to obtain reliable data for calculating service life of such wood-based products anyhow.

Besides testing efficacy of wood preservatives interest is growing for better assessment of the biological durability of wood products in general. This is not only valid when assessing the natural durability of wood species but also to evaluate modified wood (thermal and chemical modifications) and other wood treatments that can hardly show a dose response (Van Acker and Stevens 2000).

Up to now both laboratory fungal testing to assess efficacy (e.g. EN 113 and EN 807) and testing natural durability (CEN/TS 15083-1) 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 part 1 and 2 are intended as indicators for service life under specific conditions (outdoor uses 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.

EXPERIMENTAL METHODS

This paper is therefore mainly dedicated to explore the option to use the outcome of fungal testing based on a natural durability approach for assessment of the variability as factor in modelling service life prediction for thermally modified wood (Van den Bulcke *et al.* 2008).

Several durability testing experiments were performed at the Laboratory of Wood Technology at the Ghent University on timber obtained from the company Lignius. The wood modified with the SmartHeat® thermal timber treatment was assessed on its biological durability against Basidiomycetes.

The results are compared with some selected natural durability reporting as presented by Van Acker *et al.* (2010) originating from testing over the last 2 decades in the same laboratory. The wood species used for this reporting are listed in Table 1. Both temperate and tropical wood species are included as well as some softwood species. Focus has been on those species where one or limited number of botanical species is concerned (commercial samples of timber can contain more than one botanical species) and a well defined origin could be identified. It should however be stated that the sampling was not intended to cover the whole wood species variability for each of the experiments and that sometimes merely a commercial sampling was assessed. According to CEN/TS 15083-1 test specimens shall originate from a minimum of three trees or shall be taken from a stock originally of more than 500 test specimens and originating from at least five planks or boards. The tests performed on the thermally modified timber were set up according the same guidelines.

The scope of CEN/TS 15083-1 is a method for determining the natural durability of a timber against wood-destroying basidiomycetes cultured on an agar medium. The test procedure has mass loss as a criterion for assessing organism attack and the standard requires oven-dry mass to be determined. However test specimens to be used in biological tests should not be oven-dried prior to the test. More details on the procedure operations are given in Van Acker *et al.* (2010).

The classification is based on the median mass losses determined for all the test specimens exposed to each of the test fungi. The natural durability of the wood species under test in the laboratory test should be classified in accordance with Table 2.

Table 2: Classes of natural durability of wood to fungal attack using laboratory tests based on CEN/TS 15083-1

Durability class	Description	Result of laboratory tests expressed as median percentage mass loss
D1	Very durable	m.l. ≤ 5
D2	Durable	m.l. > 5 but ≤ 10
D3	Moderately durable	m.l. > 10 but ≤ 15
D4	Slightly durable	m.l. > 15 but ≤ 30
D5	Not durable	m.l. > 30

The data for each combination of wood species and Basidiomycetes test were ranked and as such used for Weibull fitting (Weibull 1951). Significant Weibull distributions are expressed and graphically presented as a probability density and as a distribution function for each data set.

The Weibull probability density function can be presented as in the below equation (Eqn. 2):

$$f(x; \lambda, k) = \begin{cases} \frac{k}{\lambda} \left(\frac{x}{\lambda}\right)^{k-1} e^{-(x/\lambda)^k} & x \geq 0 \\ 0 & x < 0 \end{cases} \quad (2)$$

where $k > 0$ is the shape parameter and $\lambda > 0$ is the scale parameter.

For each data set the (cumulative) Weibull distribution function is described as follows (Eqn.3):

$$F(x; k, \lambda) = 1 - e^{-(x/\lambda)^k} \quad (3)$$

Furthermore simple analysis allows calculating the median value $\text{Med}(X)$ and e.g. quantiles at 0.1 (10 %) $r_{0,1}$ and at 0.9 (90%) $r_{0,9}$, meaning the level at which 10 % of the specimens showed lower or higher mass loss respectively. Additionally for the mass loss ranges as identified in table 2 the percentage of the wood that can be attributed to each durability class can be derived.

RESULTS AND DISCUSSION

The figures 1 to 4 detail results from Basidiomycetes testing according to CEN/TS 15083-1. Each figure contains a graphic representation of both the probability density and distribution function for each data set. In the related table below the graphs details are given on the median value $\text{Med}(X)$, the quantiles $r_{0,1}$ and $r_{0,9}$, and percentages for each durability class using the mass loss ranges as in table 2. The rows in italic are not considered as outcome on durability according to the standard CEN/TS 15083-1 since they are not referring to the fungus showing the highest median mass loss value.

Figure 1 reports on natural durability of 4 tropical hardwood species and the softwood species Douglas fir (*Pseudotsuga menziesii*) and European larch (*Larix decidua*). These are all species commonly used or sometimes intended to be used for outdoor applications however not focussing on in ground contact situations. The tropical hardwoods sapelli (*Entandrophragma cylindricum*), tauari (*Couratari spp.*), movingui (*Disthemonanthus benthamianus*) and curupixa (*Micropholis spp.*) were all tested with *Coriolus versicolor*. Results for *Coniophora puteana* are not presented since significantly lower mass losses were recorded with this fungus. Sapelli, tauari and movingui are predominantly showing material in D4 and even over 10 % in D3. The wider distribution of sapelli and movingui also implies some 5 % of the material is classified as D5. Curupixa shows some 30 % in D5 but still close to 10 % in D3 while over 50 % is in class D4. Movingui could be classified as D3 but higher proportions of the tested material are belonging to both D2 and D4, while significant amounts are D1 and D5. This but also the other ones presented here are clearly wood species with scope for probabilistic appraisal when considering service life prediction and focussing on a median mass loss of less than 15 % (D3) which might be somewhat misleading.

Figures 2 and 3 report on some results of temperate hardwoods only for *Coriolus versicolor* (mass losses obtained for *Coniophora puteana* were anyhow lower), while Figure 4 shows data on thermally modified spruce which was tested with the fungi

Coniophora puteana and *Poria placenta*. Both the natural durability is presented as well as the enhanced durability induced by thermal modification according to the SmartHeat® thermal timber treatment. All batches were sampled as such that both untreated and modified material is fully comparable.

Ash (*Fraxinus excelsior*) (Figure 2) shows a clear shift towards higher durability classes when modified. Process mass losses (PML) of approximately 10 and 15 % brings this material already in respectively D1 and classes D2/D3 independently of leaching according to EN84 of test specimens has been part of the test or not. A low percentage of material still in D3, D4 or D5 and the low $r_{0,9}$ indicate the minimal presence of lower durability material in the treated batches.

Both beech (*Fagus sylvatica*) and maple (*Acer pseudoplatanus*) (figures not included) allow for similar conclusions for treatment levels at 5-6 % and 13-14%. All treated material shows better performance results both regarding the level of mass loss and the variability of the data when comparing with the tropical hardwood species natural durability as presented in figure 1.

Also birch (*Betula pendula & pubescens*) and poplar (*Populus spp.*), the last one being clearly a lower density hardwood, show that it is feasible to obtain thermally modified timber with very limited amount of lower durability material present. For both birch and poplar data were obtained of 2 different test sets representing each time wood from different origin. Although for birch and poplar some differences between both sets could be detected the overall increased biological durability depending on a process mass loss level is clearly present. A process mass loss of over 14 % seems to lead to TMT material with nearly only D1 and D2 specimens present and $r_{0,9}$ lower than 10%.

Regarding the 3 thermally modified softwood species: spruce (*Picea abies*) (figure 4), maritime pine (*Pinus pinaster*) and radiate pine (*Pinus radiata*) (figures not included) reference should be made to Douglas fir and larch in figure 1. Spruce (figure 4) treated at process mass loss levels of 1.6 and 3.6% allows classifying the product as respectively slightly worse or slightly better than both reference species. Maritime pine and radiate pine shows that PML levels of 9 to 10% are required to get to durability levels which classifies the TMT material in D3 or higher. It needs to be stated that although *Coniophora puteana* is more virulent in decaying the non modified material it is clearly *Poria placenta* which becomes the critical fungus to assess biological durability according to the standard CEN/TS 15083-1. Similarly as for the low variability of modified temperate hardwoods also TMT softwood shows a higher degree of homogeneity than the biological durability of Douglas fir and larch.

CONCLUSION

The methodology of the European standard CEN/TS 15083-1 uses median mass loss values recorded for the most degrading Basidiomycetes test fungus under worst case laboratory testing. This is a suitable factor to classify a sample of wood with regard to the resistance to decay either as evaluator for natural durability or enhanced durability due to thermal modification. Additional information can be obtained using the Weibull distribution and derived quantiles like those for 10% or 90%. Such results are more useful to indicate variability in expected service life. Furthermore the use of percentages attributed to different durability classes allows for a more probabilistic approach and clearly indicates to engineers to what extent thermally modified wood can be used as an alternative for medium durable tropical hardwood species or more durable softwood

species. Data obtained for a range of wood species treated with the SmartHeat® thermal timber treatment clearly shows feasibility to treat timber to a durability level based on the indicator process mass loss with a contained variability and hence allows for producing material fit for purpose.

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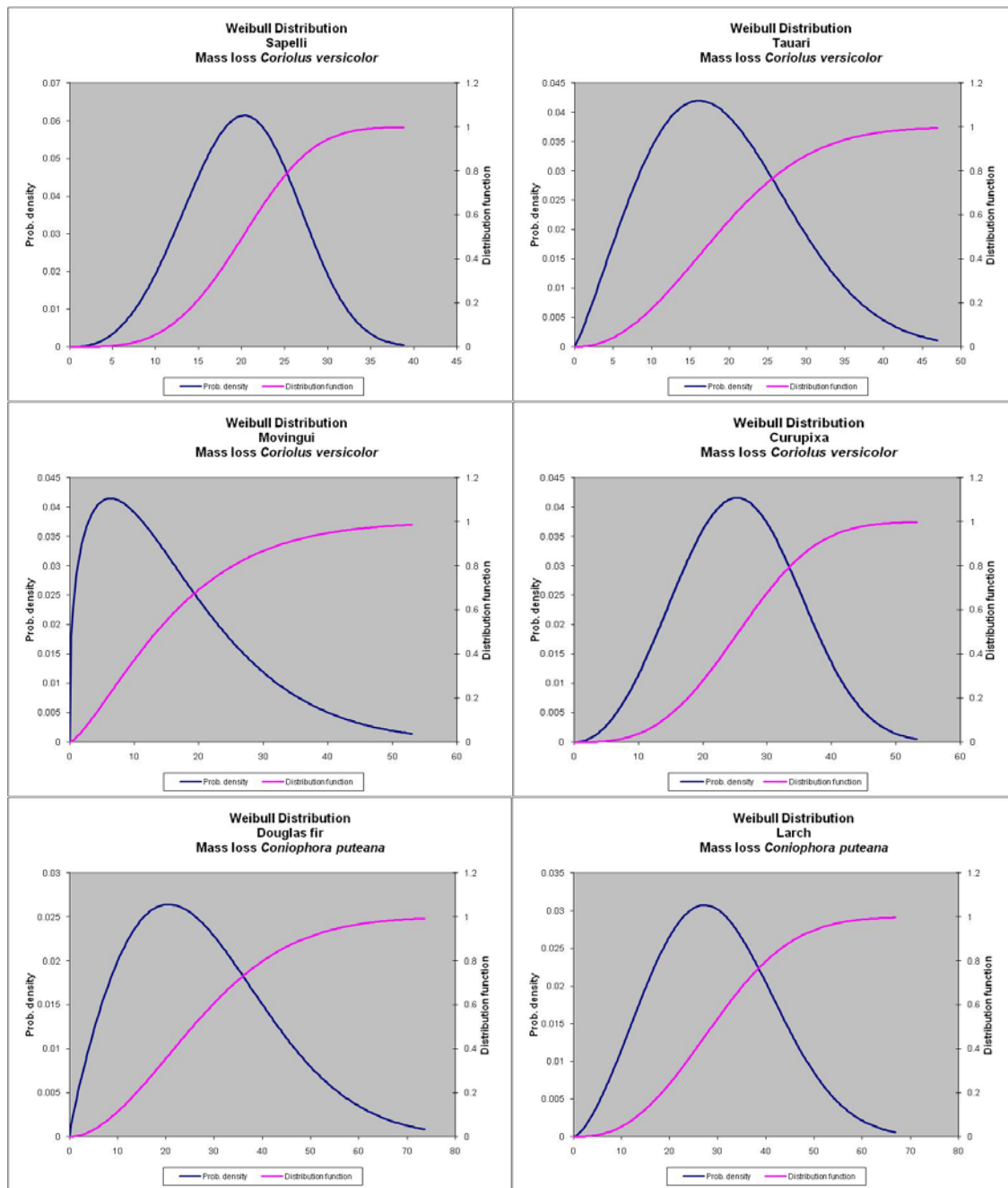
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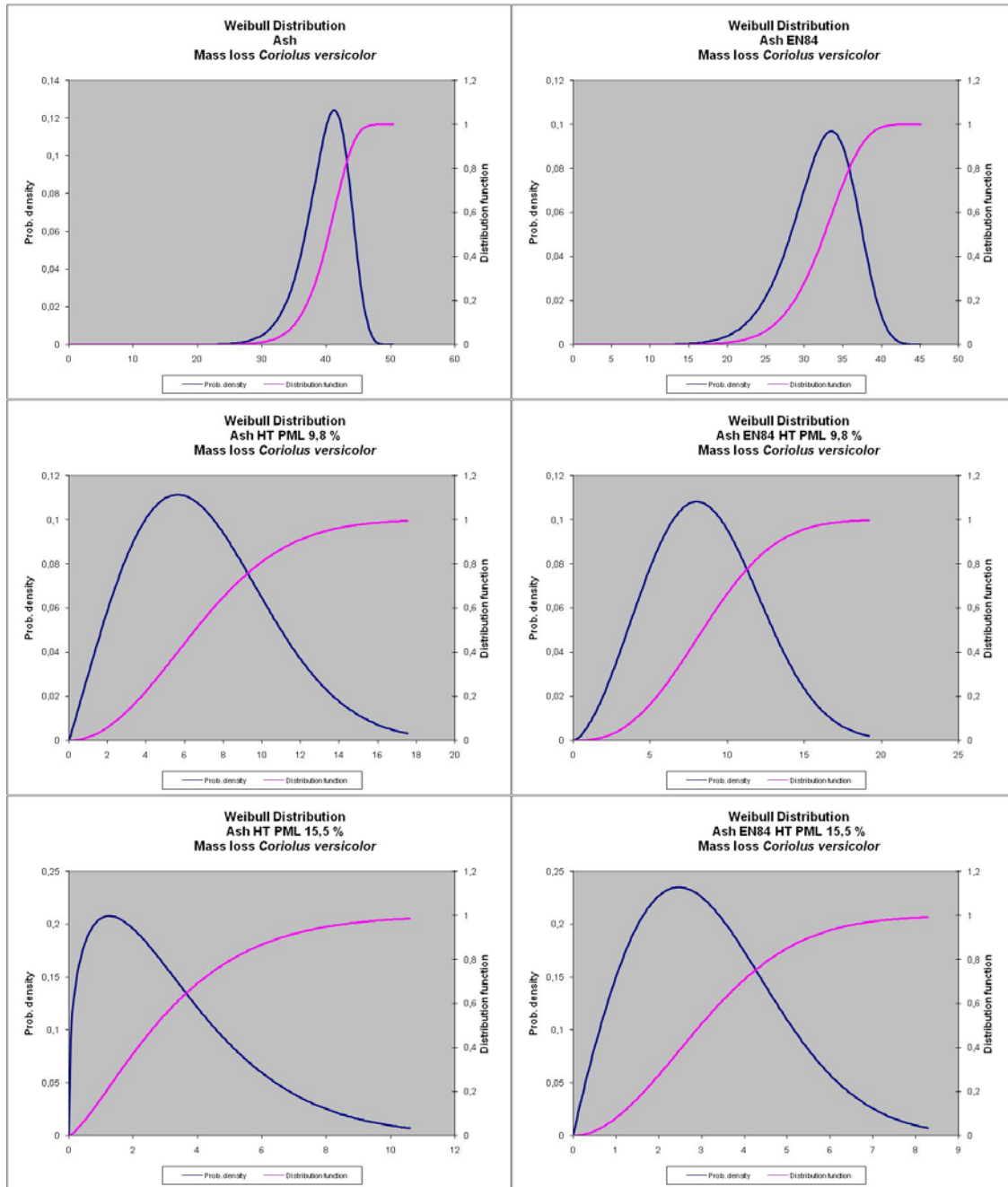
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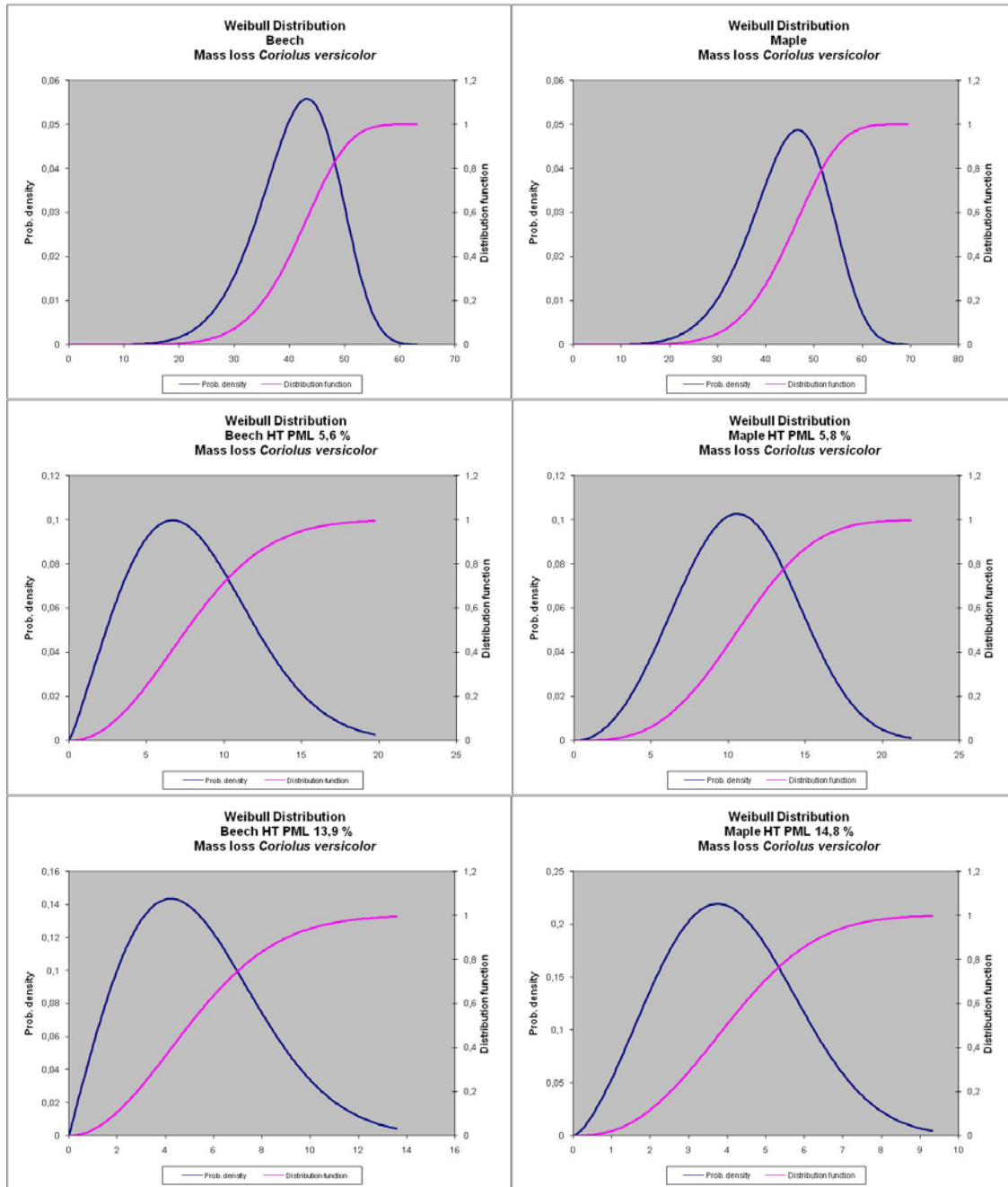
Wood species	Fungus	Med(X)	$r_{0.1}$	$r_{0.9}$	%D1	%D2	%D3	%D4	%D5
Sapelli	COR	20.1	11.8	28.2	0.5	5.1	16.1	72.7	5.6
Tauari		18.4	14.8	21.3	0.0	0.4	10.7	88.9	0.0
Movingui		20.1	11.8	28.2	0.5	5.1	16.1	72.7	5.6
Curupixa		25.5	13.8	37.8	0.5	3.4	8.8	55.2	32.1
Douglas fir	CON	25.5	9.3	48.6	3.3	8.1	11.3	38.2	39.1
Larch		28.7	13.7	46.1	0.8	3.9	7.8	41.4	46.1

Figure 1: Weibull distributions of mass loss (% , x-axis) and durability classes for medium durability tropical hardwoods (sapelli, tauari, movingui, curupixa) and for softwoods Douglas fir and European larch.



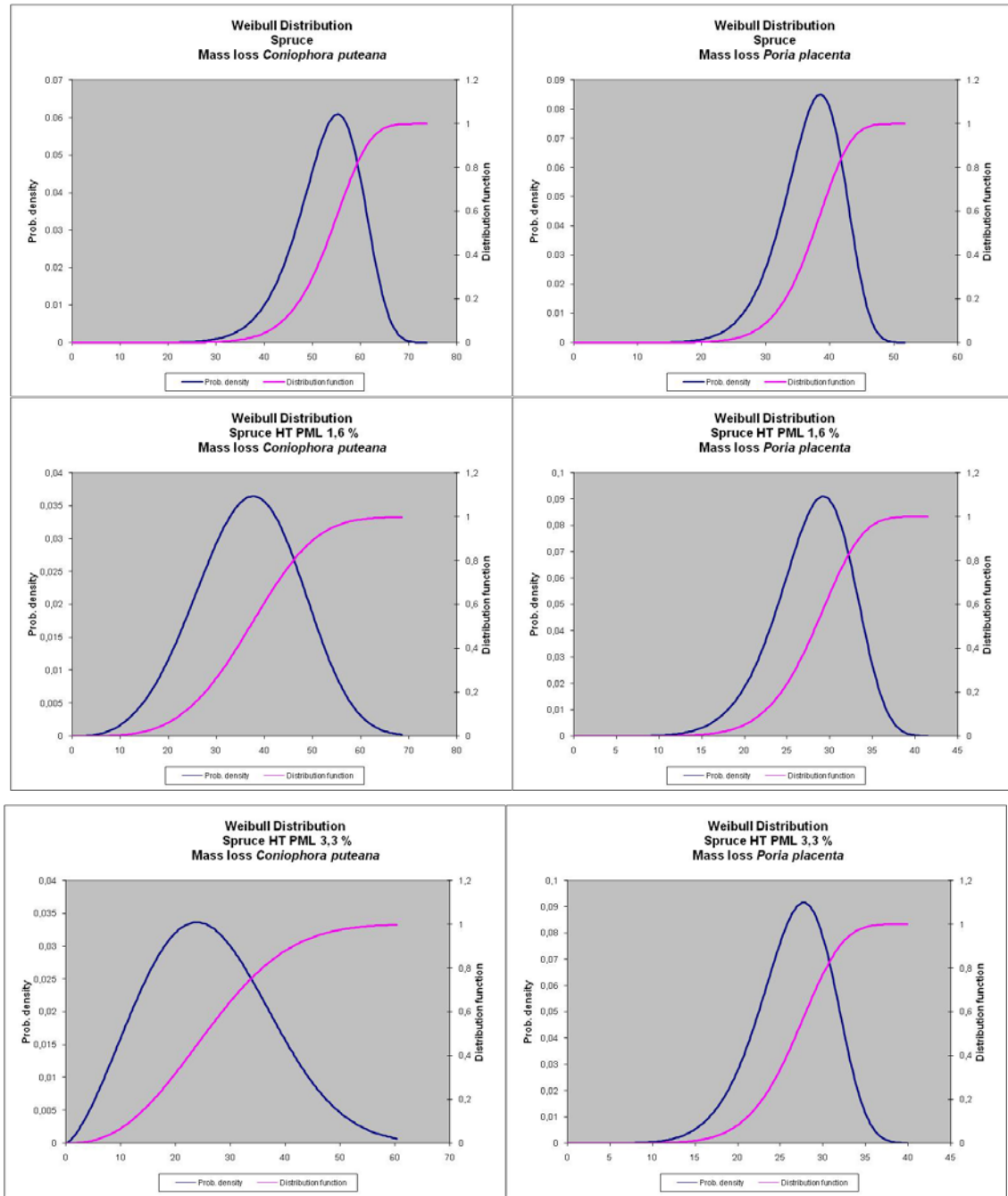
Wood species	Fungus	Med(X)	r _{0,1}	r _{0,9}	%D1	%D2	%D3	%D4	%D5
Ash	COR	40.4	35.3	44.1	0.0	0.0	0.0	1.1	98.9
PML 9.8 %		6.5	2.6	11.7	33.0	48.0	16.8	2.2	0.0
PML 15.5 %		2.7	0.7	6.6	79.6	18.6	1.7	0.1	0.0
Ash EN84		32.6	26.4	37.3	0.0	0.0	0.1	28.2	71.8
PML 9.8 %		8.4	4.1	13.3	16.4	50.1	29.2	4.3	0.0
PML 15.5 %		3.0	1.1	5.5	85.2	14.7	0.1	0.0	0.0

Figure 2: Weibull distributions of mass loss (% , x-axis) and durability classes for thermally modified ash (both not leached and leached according to EN84)



Wood species	Fungus	Med(X)	r _{0,1}	r _{0,9}	%D1	%D2	%D3	%D4	%D5
Beech	COR	41.9	31.5	50.2	0.0	0.0	0.1	7.2	92.7
PML 5.6 %		7.6	3.1	13.3	24.9	46.6	23.4	5.1	0.0
PML 13.9 %		5.0	1.9	9.1	50.3	43.6	5.9	0.2	0.0
Maple		45.2	33.5	54.8	0.0	0.0	0.1	5.1	94.8
PML 5.8 %		10.6	5.9	15.6	6.2	37.3	43.6	12.9	0.0
PML 14.8 %		4.0	1.9	6.4	70.8	29.1	0.1	0.0	0.0

Figure 3: Weibull distributions of mass loss (% , x-axis) and durability classes for thermally modified beech and maple



Wood species	Fungus	Med(X)	r _{0,1}	r _{0,9}	%D1	%D2	%D3	%D4	%D5
Spruce	CON	53.8	43.8	61.3	0.0	0.0	0.0	0.3	99.7
	POR	37.5	30.4	42.9	0.0	0.0	0.0	8.9	91.1
PML 1.6 %	CON	37.0	22.8	50.4	0.0	0.4	1.6	24.5	73.5
	POR	28.4	21.9	33.4	0.0	0.0	0.6	64.3	35.1
PML 3.3 %	CON	25.4	11.8	41.5	1.3	5.5	10.5	47.4	35.4
	POR	26.9	20.6	32.0	0.0	0.1	1.1	76.1	22.8

Figure 4: Weibull distributions of mass loss (% , x-axis) and durability classes for thermally modified spruce

Durability of Thermally Modified Timber Assortments against Fungi – Results from a 6 Year Field Test in Comparison with Results from Lab Tests

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Keywords: durability, field tests, basidiomycetes; soft rot, laboratory tests, thermally modified timber

ABSTRACT

The investigations were performed in a research project on the application of modified timber for play ground toys (run-time 2003-2006; funded by the Federal Ministry of Economic Affairs and Technology, reg. no. 206/03; see Scheiding *et al.* 2005). Beside mechanical properties, biological durability was focussed as a basic for this application. The durability of 12 industrially manufactured TMT assortments from 9 industrial processes, produced in 2003, was investigated in laboratory and field tests. These – double layer test with conditions of use class 3, EN 252 test with conditions of use class 4 – were started in 2003. After six years, experiences on the durability under outdoor conditions in ground and above ground are available and can be compared with the laboratory tests. With Scots pine, Norway spruce, beech and white ash as raw material, important wood species for thermal modification were included. It is important that all assortments were intended only for conditions of use class 3 (above ground) and not for use in ground contact. Together with the field tests, laboratory tests on biological durability according to EN 350/EN113 and ENV 807 were performed. Results were already presented at ECWM2 (Scheiding *et al.* 2005). In this paper, the current results of the field tests after nearly 6 years are presented and compared with those of the laboratory tests. Additionally, aspects of test methods and evaluation are discussed.

In lab tests according to EN 113, *Oligoporus placenta* caused a higher mass loss of TMT softwood than *Coniophora puteana* and *Gloeophyllum trabeum*. Within the lab test, two softwood assortments achieved durability class 2, two class 3 and three class 4. The hardwoods achieved durability classes of 1 and 2. Within the test against soft rot according to ENV 807, the most softwood assortments achieved durability class 3, three hardwoods durability class 1 and one hardwood class 3. A point at issue is the kind of calculation of the durability class – either according to EN 350-1 or to CEN/TS 15083 part 1 or 2. The different methods do not lead to the same evidence at any rate. Results will be presented for the tested TMT assortments. In the field test in ground contact, the references pine sapwood and beech achieved a mean life of 3 or 2 years, respectively. The most TMT assortments failed after 6 years except TMT beech. In result, TMT hardwoods achieved at least durability class 3 and TMT softwoods at least durability class 4. The results reconfirmed that lab tests allow only preliminary classifications of durability, which not necessarily corresponds to the durability under field conditions. It is strongly recommended to indicate the test method with a durability class, and to consider the use class to which the TMT is applicable.

EXPERIMENTAL

Material

12 TMT assortments from pine, spruce, ash and beech from 9 European producers (with different processes), manufactured in 2003, were tested. Specimens were taken from at least 6 boards. All assortments were provided by the producers for outdoor conditions above ground (use class 3). Sapwood of beech (*Fagus sylvatica* L.) and Scotch pine (*Pinus sylvestris* L.) were used as reference materials.

Laboratory tests against wood destroying basidiomycetes

The test was performed according to EN 113. Two specimens of thermally modified timber were placed together in one Kolle flask on a layer of malt extract agar. The specimens ($50 \times 25 \times 15$ mm³) of each assortment were cut from 3 several boards at least, and for each fungus 10 specimens were chosen. Because of that low number of replications, the test result has to be taken as screening results. Test fungi were *Gloeophyllum trabeum* DSM 3087, *Coniophora puteana* DSM 3085, for soft wood *Oligoporus placenta* FPRL 280 and for hard wood *Trametes versicolor* CTB 863A. Before the fungus test, one series were leached according to EN 84. All test flasks were incubated for 16 weeks at a temperature of 22°C and 75% relative humidity. At the end, the mycelium was removed from the specimens and the dry mass was determined.

Laboratory tests against soft rot fungi

TMT specimens with size $100 \times 10 \times 5$ mm³ were tested against soft rot according to ENV 807. Before the test, all specimens were leached according to EN 84 for 14 days. The choice of samples corresponded with the aforementioned test. A sufficient microbiological activity was proved for the substrate (garden soil) by a test with beech wood and cotton tissue. TMT specimens were taken and assessed after 16 and 24 weeks.

Field tests - test in ground

The test was performed following EN 252. Of each assortment, 20 replicate stakes of $500 \times 50 \times 25$ mm³ were placed into the ground up to the half of its length. Because of the high content of stones, the origin soil was exchanged for a low clayed top soil. As a speciality, the ground was covered with excorticate chips from softwood to simulate conditions in garden and landscape architecture. The rating of the decay by fungi after a defined scheme (Table 1) was done once a year, together with an impact test in the field.

Table 1: Rating scheme of EN 252

Rating	Classification	Definition of condition
0	No attack	No change perceptible.
1	Slight attack	Perceptible changes, but very limited in their intensity and their positional or distribution: Very superficial degradation, softening of the wood to an apparent depth of one millimetre.
2	Moderate attack	Clear changes to a moderate extent: Changes which reveal themselves by softening of the wood to a depth of approximately 2 to 3 mm over all or part of the test piece from the ground level zone and below.
3	Severe attack	Severe changes: Marked decay in the wood to a depth of 3 to 5 mm over a wide surface or by softening to a greater depth (10 to 15 mm) over a more limited surface area.
4	Failure	Rupture of the stake in the impact test at the test field.

Field tests - test above ground (double layer)

The test set-up is based on the method of Rapp and Augusta (2004). Staples of 20 stakes of $500 \times 50 \times 25$ mm³ (as of EN 252) were arranged in two horizontal layers. The upper stakes were staggered half a width to the lower, to form a water trap. The staple was placed on a rag with 10 cm distance to the ground of the wood chip covered test field. Although this test was developed to represent conditions of use class 3, these may tend to conditions of use class 4 in a limited extend, e.g. in the lateral interstices the stakes and the layers lower and between the layer with accumulations of water and dust.

RESULTS**Laboratory tests**

According to EN 350-1, the durability class is determined based on the x-value (determined from the arithmetic average of the relative mass loss for each test fungus):

$$x = \frac{\text{mass loss of test specimens}}{\text{mass loss of reference specimens}} \quad (1)$$

In difference, durability class (DC) according to CEN/TS 15083-1 results from median of the relative mass loss of the test specimens (determined for each test fungus). Classes are opposed to the corresponding range of x-value and median mass loss in table 2.

Table 2: Durability classes and corresponding

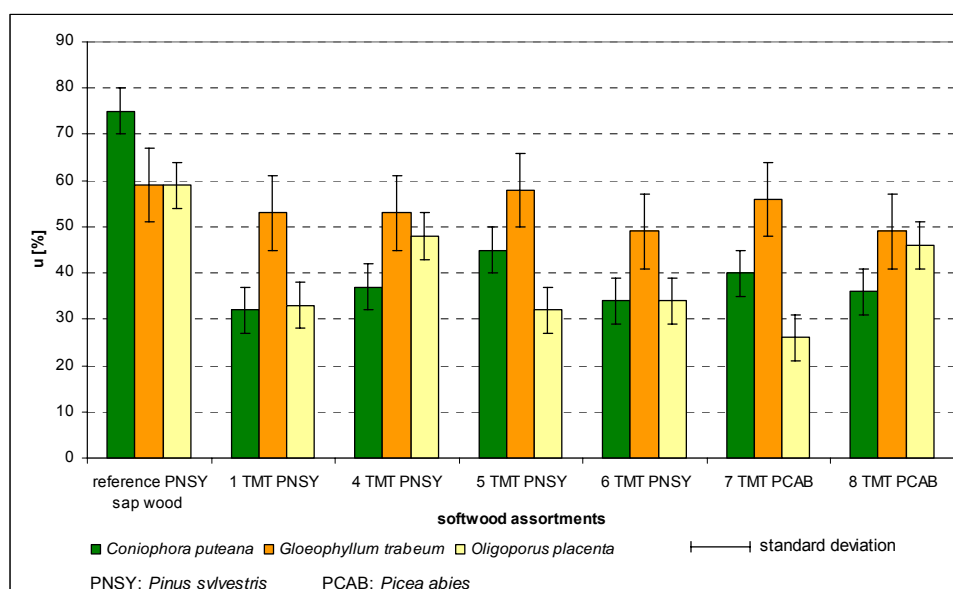
Basis for calculation	Durability class				
	1	2	3	4	5
x-value according to EN 350-1 for test against basidiomycetes and soft rot fungi	≤ 0,15	> 0,15 up to ≤ 0,30	> 0,30 up to ≤ 0,60	> 0,60 up to ≤ 0,90	> 0,90
median of relative mass loss according to CEN/TS 15083-1 for test against basidiomycetes	≤ 5 %	> 5 % up to ≤ 10 %	> 10 % up to ≤ 15 %	> 15 % up to ≤ 30 %	> 30 %

The results of lab and field tests are given in table 3. Most TMT materials from soft wood achieved DC 3 or 4, except of one TMT spruce, which gained class 2. In any case, the classification resulted from test with *Oligoporus placenta*, which caused the highest mass loss on TMT. In contrast, the untreated pine sapwood was decayed lower by that fungus than by *Coniophora puteana*. The higher virulence of *O. placenta*, comparing to other test fungi, is caused by its special enzyme system and was observed also at acetylated and some impregnated wood (e.g. Bächle *et al.* 2004; Scheiding *et al.* 2005; Ladner 2003; Welzbacher *et al.* 2004).

With resulting DC of 1 and 2, the TMT hardwood assortments achieved higher classes than the TMT soft woods (see table 3). In some cases (assortments 4, 5 and 7), the calculation following CEN/TS 15083-1 led to a better classification as calculated according to EN 113. The higher durability of the TMT hardwood (DC 1) assortments, compared to TMT softwood (predominantly durability class 3), could be confirmed in the soft rot test (ENV 807). In the fungus tests, the moisture absorption of the thermally modified wood was lower than of the untreated wood as expected. However, the values passed over 30 % in the most cases (values for TMT softwood see Figure 1). Thus, a decay by fungi was possible, and the test method could be accepted as applicable to test thermally modified timber.

Table 3: Durability classes (DC) after lab tests and 6 years field test in ground

Assortment	Producer	Wood species	DC from lab tests			DC from field test
			basidiomycetes		soft rot	
			EN 113 EN 350-1	CEN/TS 15083-1	ENV 807 EN 350-1	EN 252 EN 350-1
1	a	TMT pine	3	3	3	4
4	c	TMT pine	4	3	3	4
5	d	TMT pine	3	2	3	4
6	e	TMT pine	3	3	3	4
12	i	TMT pine	4	4	3	4
7	f	TMT spruce	2	1	2	4
8	g	TMT spruce	4	4	3	4
9	h	TMT spruce	4	4	3	4
3	b	TMT beech	1	1	1	2
10	i	TMT beech	2	2	1	3
2	b	TMT ash	2	2	3	3
11	i	TMT ash	1	1	1	2

**Figure 1: Moisture absorption of softwood assortments after 16 weeks in EN 113 test****Field tests – in ground contact**

After 6 years field test in ground, all TMT softwood assortments and two TMT hardwoods failed, so that a DC for these assortments could be determined. For references, *Fagus sylvatica* failed after 2 years and *Pinus sylvestris* after 3 years (failure criteria: 50 % of the specimens ruptured in the impact test). With a lifetime of six years, TMT hardwood achieved durability class 3, whereas TMT softwood achieved only durability class 4 at the same time. The assortments 3 (TMT beech) and 11 (TMT ash) showed very low appearances of a decay by fungi. It is expected, that these assortments with the next rating, i. e. after 7 years, will not fail and might reach at least durability class 2. The identification of the fungus species on the thermally modified timbers is going on. So far, mycelium and typical decay appearances of soft rot as well as white and brown rot fungi were found by macroscopic and microscopic observation. On the untreated references, *Bjerkandera adusta* (mainly on the in ground part of the stakes)

and *Cyathus striatus* (isolated from the transition zone between soil and air) were determined by rDNA sequencing.

Field tests – double layer test

Clear appearances of wood decay were also observed on the stakes from thermally modified timber in the double layer test. The pine and beech references failed after six years, i. e. they showed very heavy deterioration on the whole stake, e. g. in the form of brown rot. The decay on the modified assortments was clearly lower. Here, the softwood assortments showed heavier decay than the hardwoods (see table 4). It was noticeable, that the decay was initiated from the cross area in many cases. But, the heaviest decay was located between the lower and the upper layer. Often, the outside of the rack appeared intact, whereas the deterioration in the inner parts was already progressed (Figure 2). It became clear, that the stakes made from modified timber were decayed only in wetted areas, like in the interstices between the stakes and the two layers, respectively.

Table 4: Rating after 6 years in the double layer test above ground

Wood species	Assortment	Producer	Rating	Description of decomposition at the specimens
TMT pine	1	a	1.5	superficial softening, mycelium in parts
TMT pine	4	c	1.2	initiating decay from the cross area, mycelium and fruit bodies of basidiomycetes in parts
TMT pine	5	d	1.0	superficial softening
TMT pine	6	e	2.0	superficial softening, fruit bodies and brown rot at some stakes
TMT pine	12	i	1.0	superficial softening, fruit bodies in parts, heavy decay (rating number 3) on 3 stakes
TMT spruce	7	f	1.2	initiating decay from the cross area only,
TMT spruce	8	g	0.5	superficial softening, mycelium and fruit bodies of basidiomycetes in parts
TMT spruce	9	h	2.2	deep softening, mycelium and fruit bodies of basidiomycetes on many stakes
TMT beech	3	b	0.5	no decay or superficial softening, mycelium at some stakes
TMT beech	10	i	0.0	no decay
TMT ash	2	b	2.5	initiating decay from the cross area in many cases, heavy decay in parts brown rot)
TMT ash	11	i	0.5	no decay or superficial softening, heavy decay (rating number 3) on 3 stakes
beech (reference)	-	-	4.0	very heavy deterioration on the whole stake
pine sapwood (reference)	-	-	4.0	very heavy deterioration on the whole stake



*Figure 2: Appearance of TMT ash stakes from double layer test, lower layer, after 6 years:
left: lower side of the stake (facing down to the ground) without decay
right: upper side (facing to the interstice between the layers) with heavy decay*

Comparison of lab and field test results

a) Basidiomycetes lab tests EN 113 vs. CEN/TS 15083-1

After CEN/TS 15083-1 test, 2 assortments achieved one higher class than in the EN 113 test; all further 10 assortments showed the same result.

b) Soft rot lab test (ENV 807) vs. basidiomycetes lab test (EN 113, CEN/TS 15083-2)

Compared to the lab test results (lowest DC), 7 of the 12 TMT assortments got the same DC in the soft rot lab test like in the basidiomycetes lab tests; in 4 cases, one class higher, in one case, one class lower was achieved.

c) EN 252 field test vs. lab tests

Compared to the lowest DC from the 3 lab test methods, in EN 252 test, 50 % of the TMT assortments performed worse (5 assortments one class lower, 1 assortment TMT spruce two classes lower). 5 TMT assortments achieved the same DC.

d) Double layer field test vs. lab tests

In comparison of the results of the double layer test with the lab tests it is noticeable, that the results agree for the TMT beech assortments 3 and 10, which achieved high durability classes. For the softwood assortments, no clear trend is evident. However, a heavy decay in the lab test is not reflected in the double layer test.

For the individual TMT assortments, the lab tests according to EN 113, CEN/TS 15083-1 and ENV 807 showed more or less similar results. However, results varied between the softwood from class1 to 4 and at the hardwood from class1 to 3. The DC, determined by field test according to EN 252, was generally lower (in average one class) than those from lab tests. The double layer test showed a better performance of the TMT assortments than the test in ground. In both lab and field tests, TMT from hardwood performed better than TMT softwoods.

DISCUSSION

The reduced moisture absorption of thermally modified timber, one of the basic protective principles, could be confirmed within the lab tests. But, the moisture content within the lab tests exceeded values, which allow a fungal activity for wood decaying.

From the laboratory test results, a durability under conditions of use class 3, with intermittent wetting reliably, can be deduced. However, it cannot be excluded a fungus decay at a longer or permanent wetting. For these cases, as well as for an intended use in or close to ground, it is very important to consider the results from field tests. Due to different approaches of lab and field tests, it is possible to deduce a biological durability (performance) in the field from lab test results only to a certain extent. On the one hand, single species of basidiomycetes with a high decay activity are used in lab test, together with optimised living conditions. From this point of view, the exposure against fungus attack is very high in the lab. On the other hand, the exposure in the field can be even heavier due to more decaying organisms, like white and brown rot fungi, soft rot and bacteria, occur and interact. The simulation of that conditions in the lab test against soft rot fungi is limited too, although a natural soil substrate (terrestrial microcosm) is used. In contrast, the conditions in the field – especially the available moisture – are not always optimal for growth and virulence of the fungus. Thus, a field test may lead to clearly lower durability classes or vice versa, depending on the weather and climate conditions of the test period. The test field of the IHD possesses high activities of wood destroying fungi, including white rot, brown rot as well as soft rot. This exposure led to a low durability of the TMT softwood assortments. The precondition of the TMT manufacturers, not to use the products in ground contact (conditions of use class 4), could be confirmed. The TMT hardwoods performed better. In the double layer test, decay was determined at some TMT assortments, but not at all stakes. The typical starting point of the decay was the interstice between the two layers.

CONCLUSIONS

The wide range of durability classes determined for 12 TMT assortments within the different laboratory tests and field tests and the different results for each individual assortment lead to the conclusion, that it is necessary to know the based test procedure to evaluate a given durability class and to deduce a probable performance under conditions of use. In reverse, the test procedure should to be chosen in accordance with the intended application (use class). Furthermore, it is not possible to generalise the test results for thermally modified timber, but the durability is to be determined for each specific TMT assortment. For the most of the investigated TMT assortments, manufactured in 2003, the tests proved a sufficient durability for use class 3. With the new wood materials, thermally or chemically modified or treated with cross-linking and hydrophobising agents, for the determination and declaration of its biological durability arose new challenges. Additionally to the above mentioned conclusions, following facts should be considered:

- number of test standards often are unknown in practice
- use classes are much more known
- to interpret the DC better it should be known whether it was determined by lab or field tests
- DC should refer to use class 3 or 4 (others are not relevant)

Since the declaration should content more than the single figure of a durability class, as shown above, the communication of test results and durability classes should be improved. From this starting point, a simple way for declaration of DC shall be proposed:

Proposal for an improved way for declaration of durability classes

- 1) natural or biological durability class should be abbreviated with "DC"
- 2) The applicability of a DC for a use class should be given with the use class number 3 or 4.
- 3) The kind of test – lab or field – should be given by an "L" for lab and an "F" for field test.
- 4) Use class and kind of test should be added as index.
- 5) The class should be given after equal sign, for example, with **DC_{3L}=2**.

The table gives relevant tests which are applicable in principle for natural, impregnated, modified and hydrophobised wood, and the proposed declarations:

Table 5: Proposal for declaration of durability class, considering use class and kind of test

Test standard/ Test method	Keywords	Corresponding use class	Kind of test (lab or field)	Proposed declaration
EN 113	basidiomycetes	3	L	DC _{3L} =...
CEN/TS 15083-1	basidiomycetes	3	L	DC _{3L} =...
ENV 807	soft rot	4	L	DC _{4L} =...
CEN/TS 15083-2	soft rot	4	L	DC _{4L} =...
CEN/TS 12037 (lap joint)	above ground	3	F	DC _{3F} =...
double layer test (IRG/WP 04-20290)	above ground	3	F	DC _{3F} =...
EN 252	in ground	4	F	DC _{4F} =...

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Evidence for an Antioxidant Mechanism in the Durability of High-pressure Steam Modified Wood

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Keywords: Thermally modified wood, durability, ESR, antioxidants

ABSTRACT

A persistent free radical signal has been detected by Electron Spin Resonance (ESR) in high-pressure steam treated wood. The amplitude of this signal has been correlated with the reduction capacity of wood specimens towards a low ionization potential oxidant, which is a measure of antioxidant capacity of the wood specimen. The ESR-signal strength appeared to correlate also with the maximum median mass losses found in a EN113 basidiomycete durability test for a group of different heat treated softwoods as well as for a group of different heat treated hardwoods. The formation of the antioxidant capacity is proposed to be a part of a built-in defence function in natural wood against fungal decay, which could have important implications on the chemistry of wood decay.

INTRODUCTION

The changes in the chemical and related physical properties of wood heated in an oxygen-poor environment have been investigated thoroughly over the last decades (Hill 2006). The increased dimensional stability and increased durability against wood-degrading fungi (hereafter briefly: "durability") via heat treatment has found a growing volume of applications in wood industry. The market acceptance of thermally modified wood would certainly be improved when some fast method of reliable estimation of durability would become available. Preferably, such a method should be independent of the specific production process, the specific wood/tissue type and not requiring a matched reference (unheated) wood sample. A candidate method of measurement with these characteristics was found in our recent work on Electron Spin Resonance (ESR-) experiments with samples, heat treated in a high-pressure superheated steam atmosphere (Willems *et al.* 2010), although a process independence of ESR-estimated durability has yet to be verified. The mere existence of a method of direct estimation of durability of heat treated wood, independent of wood/tissue type and of untreated matched references, gives new information on the durability mechanism by heat treatment. In this paper we evaluate the ESR-results to reveal the influence of thermally generated antioxidant behaviour on the durability enhancement of wood, heat treated in high-pressure super heated steam.

EXPERIMENTAL

A brief description of the experimental details will be given here. For full details, the reader is referred to our earlier publication (Willems *et al.* 2010).

Sample preparation

Kiln dried (60°C to final moisture content 12-14% w/w) boards (26 mm thickness) of different European wood species (origin: Swiss Jura), pine, spruce, fir, beech, oak and ash, were treated in three different intensities: untreated control and high-pressure superheated steam treated at 160°C and 180°C respectively. Steam treatments were performed in WTT thermo treatment unit (DK-Brande), similar to Burmester (1973).

Durability tests

Test blocks with sizes following European Standard EN113 (15 x 25 x 50 mm³) were cut from all boards in different zones (sapwood, heartwood, transition zone) for fungal tests. All test blocks were exposed to a leaching treatment according to EN 84, conditioned to constant mass in a 20°C and 65% relative humidity climate chamber, vacuum-sealed, sterilized by Gamma-radiation and kept in the vacuum seal until inoculation with the test fungus. All wood species were tested against *Coniophora puteana*, *Gloeophyllum trabeum* and *Serpula lacrymans* as well as against *Poria placenta* for softwood species and *Coriolus versicolor* respectively for hardwood species. Ten to fifteen replicates per treatment and wood species were used for exposure to each fungus. Pine sapwood and beech were taken as reference species.

One-litre capacity glass jars filled with 4% malt agar were inoculated with mycelium of actively growing test fungi. As soon as the fungus had totally covered the culture medium, 3 wood specimens per jar (untreated, thermally treated at 160°C and at 180°C) were placed on silicon stripes to avoid direct contact with the fungal mycelium. After 16 weeks incubation time at 22 °C and 70 % RH, wood blocks were removed from the jars, carefully cleaned from adherent mycelium, weighed, oven dried at 103°C for 24 hours and weighed again to determine the mass loss. The mass loss of each specimen was calculated as a percentage of the initial dry mass.

Electron Spin Resonance

From the little available remaining material after preparation of the EN113 test blocks, 19 different pieces were recovered for the preparation of ESR-samples (Table 1). Due to the lack of any hardwood sample treated at 160 °C to correlate with the basidiomycete test results (Figure 3) interpolated ESR-values were used. Wood particles were obtained by using a hand-file avoiding excessive heat production that would induce significant levels of new stable free radicals.

The ESR measurements were performed with a Miniscope MS-200 X-band spectrometer (Magnettech GmbH, D-Berlin; magnetic field 3354.26 Gauss; Sweep 117.73 Gauss; Sweep time: 120 sec; Time constant: 0 sec; Pass number: 3; Modulation: 5000mG; Microwave power: 40dB; Gain: 500). A minimum of 100 mg dry wood particles were used into the quartz sample tube. The peak-to-peak amplitude of the first derivative signal is taken as a measure of the total number of radicals in arbitrary units. After the ESR-measurement, the dry weight of the sample was determined as the residual weight after drying at 103°C to determine the specific stable free radical density of each sample in arbitrary ESR amplitude units per gram dry weight.

	Species	Zone	Treatment		Species	Zone	Treatment
1	Beech	sapwood	--	9	Pine	sapwood	--
2	Beech	sapwood	180 °C	10	Pine	sapwood	160 °C
3	Beech	heartwood	--	11	Pine	sapwood	180 °C
4	Beech	heartwood	180 °C	12	Spruce	sapwood	--
5	Ash	transition	--	13	Spruce	sapwood	160 °C
6	Ash	transition	180 °C	14	Spruce	heartwood	--
7	Oak	heartwood	--	15	Spruce	heartwood	160 °C
8	Oak	heartwood	180 °C	16	Spruce	heartwood	180 °C
				17	Fir	sapwood	--
				18	Fir	sapwood	160 °C
				19	Fir	sapwood	180 °C

Table 1: Specification of the 19 different specimens, characterised by both ESR and basidiomycete durability tests.

Antioxidant capacity measurements were performed by measuring the triplet ESR-signal of 1ml 5 μ M TEMPOL (4-hydroxy-2,2,6,6-tetramethylpiperidine-1-oxyl) oxidant being reduced by 150 mg suspended wood particles after 10 minutes incubation time.

RESULTS AND DISCUSSION

Electron Spin Resonance (ESR)

The ESR measurement is solely sensitive for unpaired electrons, which makes it the ultimate technique to study radicals, transition metal ions and charged molecular complexes (Weil *et al.* 1994). Radical species are generally short-lived because of their extreme reactivity, but some biological matter is known to possess extremely long-lived radicals (Rex 1960). Native wood has no organic stable free radicals, but they can under certain circumstances (light exposure (Kalnins *et al.* 1966), alkaline treatment (Steelink 1966)) be reversibly generated. Under more severe treatment conditions (oxidation, heat, mechanical) the ESR-signal from stable free radicals can become persistent (Sivonen *et al.* 2002).

The ESR signal measured in samples taken from untreated pine (max temperature 60C on drying), and high pressure superheated steam-treated pine at two different treatment intensities (160 and 180°C), approximately 10 months after the heat treatment, show a broad singlet resonance (Figure 1). The signal strength in untreated pine was due to dissipated heat during sample preparation (Willems *et al.* 2010). The increasing ESR-signal amplitudes with increasing treatment intensity were consistently measured in all wood species/tissue types, in accordance with measurements on dry heated specimen (Sivonen *et al.* 2002).

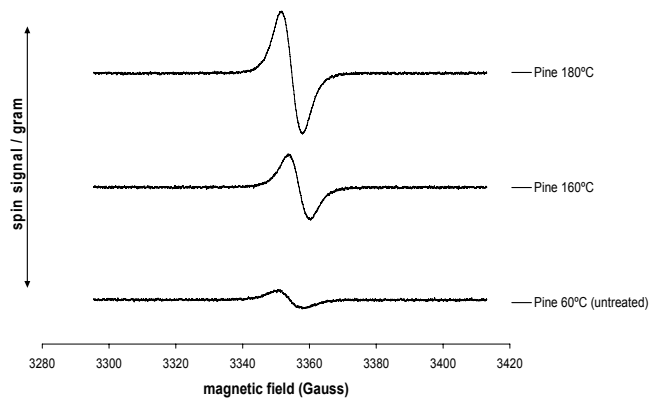


Figure 1: Measured first-derivative ESR signals from pine sapwood, ten months after heat treatment at the temperatures indicated. The amplitude of the signal increases with treatment temperature due to thermally generated persistent free radicals. Each signal has been normalized to the dry weight of the corresponding sample and then vertically shifted for separation.

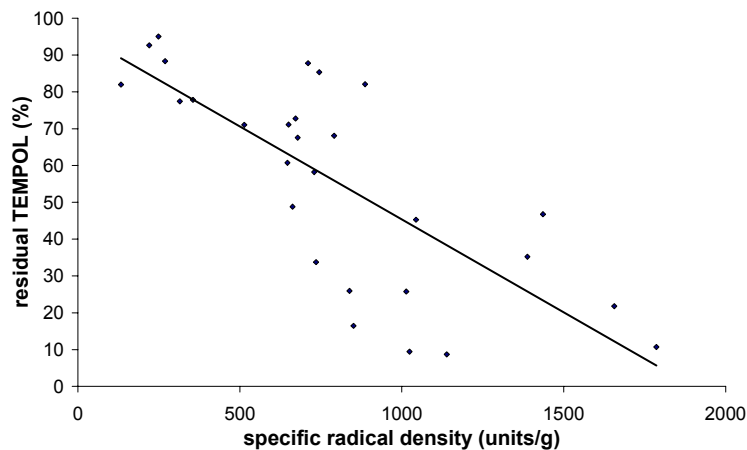


Figure 2: The residual amount of the oxidant TEMPOL as a function of the specific radical density for ash, oak, and spruce samples, treated at various temperatures and different wood moisture contents. The least square linear fit is also indicated.

Reversible stable organic radicals are most likely phenoxy radicals (Kuzina *et al.* 2004), whereas the observed persistent ones are probably of a semiquinone type (Steelink 1966, Senesi 1990). In soil science, similar radicals have been observed in the oxidized lignin-melanin fractions of humic substance in increasing concentrations with the degree of humification. The degree of humification is in turn correlated with the antioxidant capacity of humic matter, which may explain its recalcitrance (Rimmer 2006). The light absorption, fluorescence, paramagnetic (ESR-) properties of soil and laccase treated thermomechanical pulp lignin reveal striking analogies (compare Sławińska *et al.* 2007 and Barsberg and Thygesen 1999), suggesting that severe heat treatment of wood (leading to persistent radicals) may also lead to antioxidant properties. This is confirmed by antioxidant measurements on heat treated pine (Long *et al.* 2004), as well as heat treated spruce and beech (Ahajji *et al.* 2009). As a measure of antioxidant capacity, we measured the consumption of a test oxidant TEMPOL during a 10 minute incubation with powdered wood samples of high-pressure superheated steam treated spruce, ash and oak at various treatment temperatures and moisture contents and correlated it with the amplitude of the corresponding initial wood stable radical ESR-signal. The result shows a linear relationship between the consumed amount of oxidant and the stable radical density by the heat treatment, confirming antioxidant behaviour in high-pressure superheated steam treated wood (Figure 2).

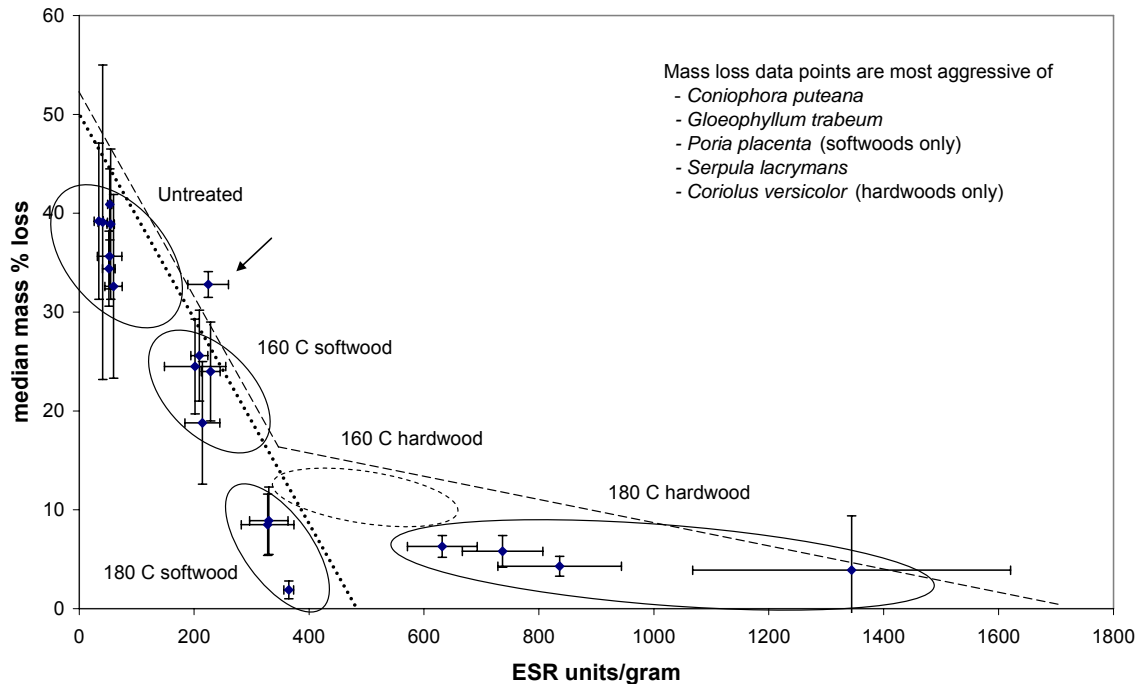


Figure 3: Relative median mass loss after 16 weeks exposure by the most aggressive of four basidiomycetes versus the ESR-signal strength in arbitrary units normalized to dry mass. Note that the 160oC treated hardwood group contains no data points, see text. The dotted line is an apparent upper limit for softwood mass loss data points. The two-sectioned broken line represents the apparent upper limit for the hardwood mass loss data points. The anomalous data point indicated with the arrow belongs to untreated ash with an exceptionally high ESR-signal strength

ESR - Basidiomycete decay resistance correlation

It is interesting to correlate the antioxidant capacity (as measured by the stable free radical density) with the median wood mass losses measured from a basidiomycete exposure test (Figure 3). Samples are grouped in sets of equal treatment intensities (process settings) and show general trends for hardwoods and softwoods respectively. Note, that within the hardwood and softwood groups we have used very different wood species and different tissue types, still showing a general correlation. This feature has never been observed before in any other kind of correlation between basidiomycete test results and physical/chemical properties of heat treated wood.

The most aggressive fungus on all heat treated hardwood samples was the white rot fungus *Coriolis versicolor*, whereas the most aggressive fungus on all heat treated softwood samples was the brown rot fungus *Poria placenta*. The different correlations found for hardwoods and softwoods may be related to the different modes of decay for these basidiomycetes. The relative independence of the correlation for different wood species and tissues within the hardwood and softwood groups indicates that antioxidant behaviour is a necessary property for durability enhancement of heat treated wood, suppressing or delaying the non-enzymatic attack of fungi on the wood matrix.

The conclusion of an antioxidant mechanism in the durability of heat treated wood, as follows from our measurements, is quite unconventional. Commonly, the durability

enhancement of heat treated wood has been attributed to the removal of hemicelluloses (Rowell *et al.* 2009) and/or to the reduced equilibrium moisture content (Tjeerdsma *et al.* 1998). On the other hand, antioxidant variations have been shown to explain the variability of natural durability of Scots pine (Harju and Venäläinen 2006). A positive effect of natural and synthetic antioxidants on natural durability of heartwood has also been shown (Schultz and Nicholas 2000), but antioxidants are unlikely the sole cause of durability against basidiomycetes (Green III and Schultz 2003).

Hypothesis on the biological origin of the durability mechanism in thermally modified wood

On comparison of the chemical changes during thermal modification of wood and those seen during fungal decay, some striking similarities become apparent: hemicelluloses and lignin depolymerization, demethoxylation/demethylation of lignin monomers, repolymerization, formation of new carbonyl moieties (Tjeerdsma *et al.* 1998, Fengel and Wegener 1989) as well as the formation of stable free radicals (Pearce *et al.* 1997, Sivonen *et al.* 2002). Since we know that heat treatment can effectively improve the resistance of wood against basidiomycetes, the chain of chemical reactions triggered by heat treatment might represent a built-in defence mechanism that is also activated during an oxidative attack on wood during the incipient phase of fungal decay. If this is true, the observed chemical changes would be caused (at least for a significant part) by a physiological reaction of the wood itself, rather than by the fungus.

There is a defence system activated after wounding and fungal infection of the stem of living trees, leading to a compartmentalization around the infected area before the fungus has fully colonized this confined region (Pearce *et al.* 1997). Wood chemical reactions within this compartment lead to the formation of fungicidal phenolic compounds and stable free radicals, acting against the pathogen. The blocking efficiency towards fungal hyphae on crossing the boundary cells of the confinement relies on water saturation of the cell lumina. Dry timber has by definition no water saturated cell lumina as barriers against fungi, but heat treatment will activate the defence mechanism over the entire volume of the wood before any fungal infection has occurred.

An analogy between heat treatment and oxidative fungal attack on wood could explain the fact why a seemingly simple heat treatment is effectively capable to provide a significant degree of improvement in the resistance against all wood-degrading fungi and on all types of wood, because it is an evolutionary optimized mechanism. It can also shed light on the difference between selective white rot and simultaneous white rot decay (Arantes *et al.* 2010): the latter proceeds by gradual erosion of the wood polymers by high molecular weight enzymes at the surface of the cell wall, thereby avoiding triggering the proposed defence mechanism when small oxidizing species would diffuse into the cell wall.

CONCLUSIONS

In this research, ESR-measured persistent free radical signals in high-pressure superheated steam treated wood are shown to reflect proportional antioxidant capacity, which in turn give general trends with the median mass losses measured for a group of three different hardwoods as well as for a group of three softwoods. Species and tissue

type independence within these groups suggest the direct involvement of antioxidant capacity in the mechanism of durability by heat treatment.

The formation of antioxidant capacity is a result of a chain of wood chemical reactions which may be sensitively triggered thermally or by oxidation during incipient decay, providing a built-in defence action against decay in living trees. This evolutionary optimized defence system could explain the remarkable efficacy of heat treatments with practically all wood species and types of wood degrading fungi.

During incipient fungal decay the proposed defence system may be activated to bring about significant chemical changes which are caused by the wood itself rather than the fungus.

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Prediction of Decay Resistance of Different Softwood and Hardwood Species after Heat Treatment Based on Analysis of Wood Elemental Composition

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ABSTRACT

Wood heat treatment is an attractive alternative to improve decay resistance of low natural durability wood species. Decay resistance is strongly correlated to thermal degradations of wood cell wall components. Some recent studies proposed the use of wood elemental composition as a valuable marker to predict final properties of the material. These results, initially obtained with pine, have been extended to different softwood and hardwood species to check validity of the method using equipment specially conceived to measure mass losses during thermal treatment. Heat treatment was performed on two softwood species (pine and Silver fir) and tree hardwood species (poplar, beech and ash) at 230°C under nitrogen for different times to reach mass losses of 5, 10 and 15%. Heat treated specimens were exposed to fungal decay using the brown rot fungus *Poria placenta* and the weight losses due to fungal degradation determined as well as initial wood elemental composition. Correlations between weight losses recorded after fungal exposure and elemental composition indicated that carbon content or O/C ratio can be used to predict wood durability conferred by heat treatment. Moreover, it was observed that for given curing conditions thermo-degradation patterns of the different samples differed considerably according to the wood species. The sole analysis of wood physical properties like its density, thermal conductivity and diffusivity cannot allow explaining the observed differences, which should also depend of thermally activated chemical processes depending of wood chemical composition.

INTRODUCTION

Nowadays, the use of wood as building material is subjected to increasing interest due to its intrinsic properties and its ability to fix carbon dioxide. Wood heat treatment by mild pyrolysis has been reported to improve some of its properties such as its biological durability (Kamdem *et al.* 2002, Hakkou *et al.* 2006) and its dimensional stability (Mouras *et al.* 2002). This process avoids the use of wood preservatives, which enables the treated wood to remain an environmentally friendly product. The influence of treatment conditions on chemical composition and conferred properties of heat-treated wood have therefore been intensively investigated. Wood heat treatment induces chemical modifications of the main wood constituents. The lignin polymer network is modified (Zaman *et al.* 2000, Tjeerdsma and Militz 2005, Nguila *et al.* 2006, Nguila *et al.* 2007a), the ratio between amorphous and crystalline cellulose is also changed (Fengel and Wegener 1989, Sivonen *et al.* 2002, Yildiz *et al.* 2006), hemicelluloses are

strongly degraded (Sivonen *et al.* 2002, Nuopponen *et al.* 2004, Gérardin *et al.* 2007), some products precursors of the charcoal appear (Nguila *et al.* 2007b). Different heat treatment conditions have been described in the literature (Militz 2002, Patzelt *et al.* 2002). Among these, the wood torrefaction corresponds to heat treatment carried out at temperatures inferior to 300°C under inert gaseous atmospheres. Chemical reactions involved during torrefaction as well as final properties of the material depend strongly on the treatment temperature and of its duration. During torrefaction, wood is thermally decomposed at a slow rate (Degroot *et al.* 1988). Recently, it was reported that the anhydrous mass loss during the heat treatment could be a reliable and accurate marker to predict decay resistance of heat-treated wood (Hakkou *et al.* 2006, Welzbacher *et al.* 2007). Hence, the control of the mass of the material during the heat treatment process will allow predicting its final durability. Due to the importance of dehydration reactions occurring during the heat treatment, the behaviour of carbon and oxygen contents have been evaluated through determination of wood's elemental composition (Nguila *et al.* 2009) and reactivity of free hydroxyl groups with acetic anhydride (Nguila *et al.* 2007a). Indeed, previous studies have shown that heat treatment resulted in numerous dehydration reactions due to degradation of amorphous polysaccharides (Fengel and Wegener 1989, Sivonen *et al.* 2002, Yildiz *et al.* 2006) jointly with the formation of carbonaceous materials within the wood structure leading to a strong decrease of wood's O/C ratio (Nguila *et al.* 2006, Nguila *et al.* 2007b). Moreover, dehydration reactions occurring during heat treatment have been reported to be at the origin of the lower reactivity of hydroxyl groups of wood cell wall polymers during acetylation (Tjeerdsma and Militz 2005, Nguila *et al.* 2007a). The purpose of this study is to evaluate the correlations between the improvement of the durability of different softwood and hardwood species and the mass losses induced by the heat treatment estimated on the basis of their O/C ratio.

EXPERIMENTAL

Heat treatment

Samples were cut from heartwood boards of different softwood and hardwood species: beech, *Fagus sylvatica L.*; poplar, *Populus nigra*; ash, *Fraxinus excelsior L.*; pine, *Pinus sylvestris* and Silver fir, *Abies pectinata*.

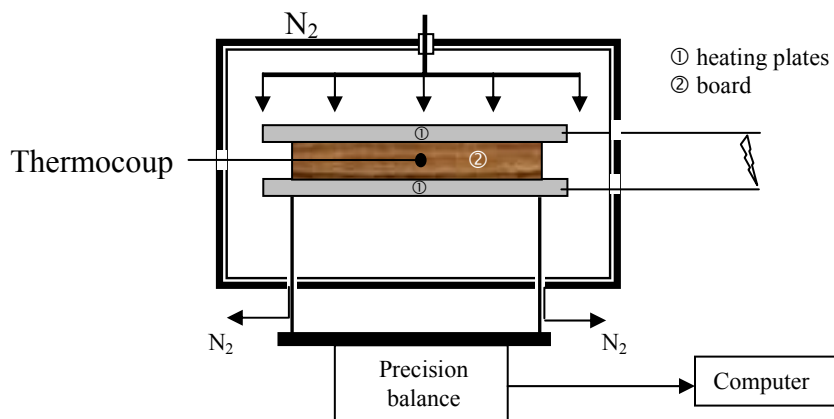


Figure 1: Schematic equipment used for heat treatment.

Heat treatment was performed under nitrogen on the different species by conduction between two metallic heating plates placed on a precision balance allowing recording of

dynamic mass loss as a function of time and temperature (Figure 1). Dimension of the boards used for heat treatment were 2.5 x 11x 25 cm³ (R, T, L). Wood specimens were oven dried at 103°C during 48 h prior to heat treatment. Weight of the sample was recorded automatically all along the experiment and mass loss due thermo-degradation calculated according to the formula (Eqn. 1) :

$$ML (\%) = 100 \times (m_0 - m_1) / m_0 \quad (1)$$

where m_0 is the initial oven dried mass of the sample before heat treatment and m_1 the oven dried mass of the same sample after heat treatment.

Microanalysis

Wood was grounded to fine sawdust and passed through different sieves to obtain a powder of granulometry comprised between 0.2 and 0.5 mm. Sawdust was conditioned at 103°C for 24 h. and stored in closed bottle before analysis. Elemental analyses were performed on a Thermofinnigam Flash EA1112 micro-analyser.

Fungal durability

Wood blocks of 5 x 10x 30 mm³ were cut from heat treated boards for fungal durability evaluations. Petri dishes (9 cm diameter) were filled with sterile medium (20 mL) prepared from malt (40 g) and agar (20 g) in distilled water (1 L) and inoculated with a piece of mycelium of a freshly grown *Poria placenta* culture. Petri dishes were incubated at 22°C and 70% HR until full colonization of the surface's medium by the mycelium. Two heat treated specimens and one untreated sample were placed in each Petri dishes and exposed to the brown rot fungus for 16 weeks. Each experiment was duplicated. At the end of test period, mycelia were removed and the blocks were dried at 103°C and weighed (m_2) to determine the weight loss caused by the fungal decay (Eqn. 2) :

$$WL (\%) = 100 \times (m_{0 \text{ or } 1} - m_2) / m_{0 \text{ or } 1} \quad (2)$$

where $m_{0 \text{ or } 1}$ are respectively the initial oven dried mass of untreated or heat treated wood blocks before fungal exposure and m_2 is the oven dried mass after fungal attack.

RESULTS AND DISCUSSION

Mass losses of the different wood species as a function of time are presented in figure 2 for similar curing conditions. Mass loss depends of the density but also of the nature of the wood species. Until 160°C, only very small mass losses were observed corresponding to vaporization of volatile extractives and of bound water absorbed on the wood fibres. Thermo-degradations begin at higher temperatures and are effective at 230°C. Species of lower density present better stability to thermo-degradation than species of higher density. A first attempt to explain this difference is associated to intrinsic thermal properties of each wood species. Indeed, the phase of heat transfer may differ according to thermal properties of each species limiting thermo-degradation reactions.

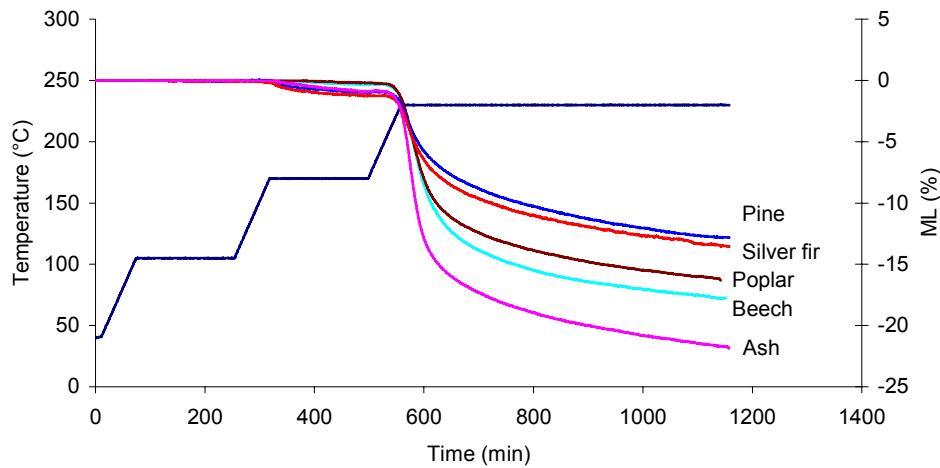


Figure 2: Evolution of mass during heat treatment of different wood species.

Diffusivity α ($\text{m}^2 \cdot \text{s}^{-1}$) is calculated from the following relation (Eqn. 3) :

$$\alpha = \lambda / \rho \cdot C_p \quad (3)$$

where λ is the conductivity ($\text{W} \cdot \text{m}^{-1} \cdot \text{K}^{-1}$) given by literature, ρ the density ($\text{kg} \cdot \text{m}^{-3}$) measured for each wood species, and C_p the specific heat, which depend of the temperature according to the formula (Eqn. 4) where T is the temperature in Kelvin.

$$C_p = 1112 + 4,85 (T - 273) \quad (4)$$

Due to the transient mode during heat treatment, it is difficult to determine diffusivity with precision. Indeed, all parameters vary with time and temperature as the thermo-degradation reactions take place, so that it was difficult to evaluate diffusivity. For these reasons, diffusivities were calculated for each wood species at the beginning and at the end of the treatment. Data are given in table 1.

Table 1: Thermal properties of the different wood species before and after thermal treatment at 230°C.

Species	Density ($\text{kg} \cdot \text{m}^{-3}$)		Conductivity ($\text{W} \cdot \text{m}^{-1} \cdot \text{K}^{-1}$)		Diffusivity ($\text{m}^2 \cdot \text{s}^{-1}$)	
	before	after	before	after	before	after
Beech	653	591	0.1544	0.1420	$1.06 \cdot 10^{-7}$	$1.08 \cdot 10^{-7}$
Poplar	437	394	0.1112	0.1026	$1.14 \cdot 10^{-7}$	$1.17 \cdot 10^{-7}$
Ash	675	589	0.1588	0.1416	$1.06 \cdot 10^{-7}$	$1.08 \cdot 10^{-7}$
Pine	461	439	0.1160	0.1116	$1.13 \cdot 10^{-7}$	$1.14 \cdot 10^{-7}$
Fir	447	410	0.1132	0.1058	$1.14 \cdot 10^{-7}$	$1.16 \cdot 10^{-7}$

Beech and ash, which present the higher densities and conductivities and lower diffusivities are degraded more rapidly, while pine, fir and poplar which present the lower densities and conductivities and higher diffusivities are less susceptible to thermo-

degradation. However, other parameters should be involved to explain the differences observed between the two softwoods species and poplar, which present quite similar thermal properties but different thermo-degradation patterns. Softwoods and hardwoods differ in the percentage and the composition of hemicelluloses. Softwoods contain galactoglucomannan and arabinoglucuronoxylan, while hardwoods contain mainly glucuronoxylan and low amount of glucomannan. Moreover, xylan units of hardwood glucuronoxylan are strongly acetylated, comparatively to softwood hemicelluloses for which acetyl groups are attached to the glucomannan backbone (Sjöström 1981, Fengel and Wegener 1989). Deacetylation of hemicelluloses causes liberation of acetic acid, which catalyses depolymerisation of the less ordered carbohydrates like hemicelluloses and amorphous cellulose. Higher content of acetyl groups present in hardwoods may be at the origin of the higher kinetic of thermo-degradation observed for poplar comparatively to softwoods species. Similarly, differences in chemical composition should be involved to explain differences of thermo-degradation patterns observed for beech and ash, which present quite similar densities and diffusivities. Starting from thermo-degradation curves, it was possible to estimate curing times to reach a given mass loss. Each wood species was heat treated during different times to reach mass losses of approximately 5, 10 and 15%. Elemental composition and durability against the brown rot fungus *Poria placenta* were then measured. Correlation between mass losses and carbon content is presented in figures 3.

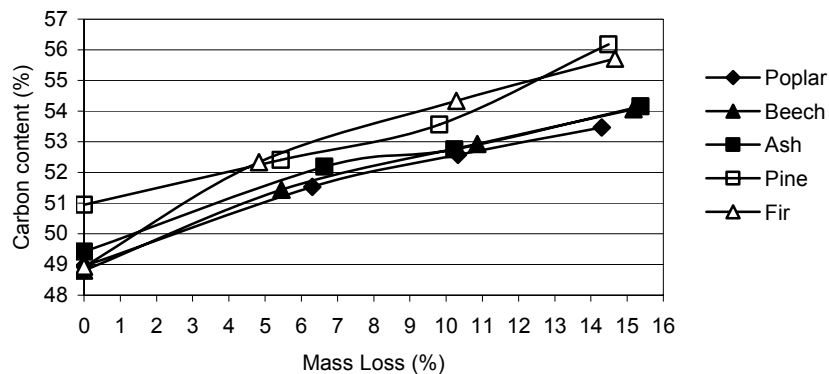


Figure 3: Correlation between mass loss resulting from heat treatment at 230°C and carbon content for different wood species.

As expected, wood carbon content increases as the mass loss increases, while oxygen content decreases (Nguila *et al.* 2009). For a similar mass loss, softwoods present higher carbon content than hardwoods. In all cases, evolution of carbon content increases linearly as the mass loss increases showing a good correlation between mass loss and carbon content. Even if the kinetics of thermo-degradation are different, their effects on wood chemical composition for a same level of degradation are relatively close. This is not surprising considering that the main modifications occurring during wood heat treatment are due to degradation of hemicelluloses through depolymerisation reactions to C5 and C6 monosaccharides leading after dehydration to furfural, hydroxymethylfurfural or levoglucosenone. These products may either be lost by evaporation or subject to further degradation leading to furan, formaldehyde, formic acid, levulinic acid and other by-products involved in thermo-condensation or thermo-reticulation with lignin. From a chemical point of view, it seems reasonable to think that quite similar products were formed for a similar mass loss making abstraction of the initial chemical differences existing between softwoods and hardwoods. The main

difference concerns the kinetic of thermo-degradation, which differs significantly between softwoods and hardwoods. This difference may be explained by the higher acetyl content present in hardwoods leading to the formation of higher quantities of acetic acid involved in acidic catalysis of hydrolysis and dehydration reactions, but also by the higher susceptibility to hydrolysis of pentoses present in hardwoods hemicelluloses (Xu *et al.* 2009). Correlations between mass loss and O/C ratio are shown in figure 4.

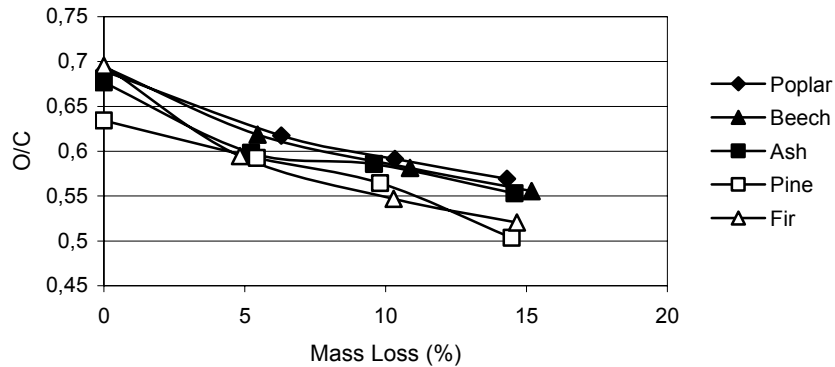


Figure 4: Correlation between mass loss resulting from heat treatment at 230°C and O/C ratio for different wood species.

O/C ratio decreases linearly with the increase of the mass loss indicating that O/C ratio could be a valuable marker of heat treatment intensity. This decrease can be mainly attributed to thermal degradation of wood mentioned above and subsequent dehydration reactions explaining the decrease of oxygen content. Even if each wood species presents different behaviour, the tendencies observed remained the same indicating formation of degradation products with relatively similar structures. Except for untreated fir, higher atomic O/C ratios were obtained with hardwoods. This observation can be explained by the higher syringyl content of hardwoods lignins compared to softwoods, which contain mainly guaiacyl units. Similarly to our previous results obtained with pine, the strong correlations observed between mass losses due to thermal degradations and O/C ratios allow envisaging O/C ratio or carbon content as valuable markers of the heat treatment intensity.

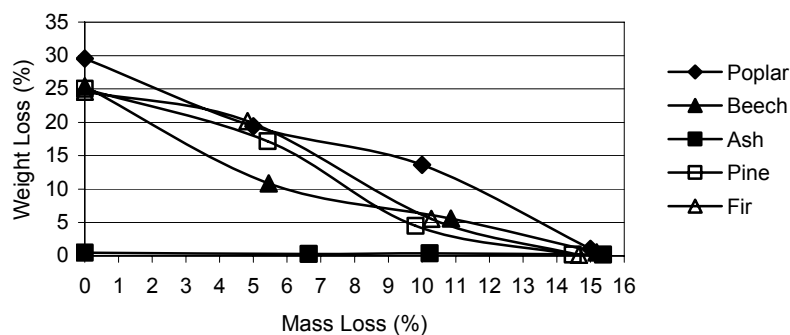


Figure 5: Correlation between mass loss resulting from heat treatment at 230°C and weight loss due to fungal degradation for different wood species.

Correlation between mass loss due to heat treatment and weight loss due to fungal degradation are shown in figure 5. Except in the case of ash, which was totally resistant to *Poria placenta*, all wood species present weight losses in direct connection with their degree of thermo-degradation. Similarly to our previous results obtained with pine,

conferred durability increase with treatment intensity. Independently of the wood species used, wood samples become totally resistant to decay for mass losses around 15%. This value can be associated to a carbon content of approximately 56% for softwoods and 54% for hardwoods, confirming the possibility to use wood elemental composition as a marker to predict decay durability of heat treated wood.

CONCLUSIONS

The results of this study have made obvious that there isn't any simple relation between the wood's thermal characteristic and the thermo-degradation mechanism. Even if wood species of lower densities seems to be more resistant to thermodegradation, other parameters should be involved to explain difference in thermodegradation patterns observed between softwood and hardwood of similar densities or hardwoods of similar densities. The kinetic of the mass loss during the heat treatment is strongly related to the wood composition and particularly to its content of acetyl groups. The study has also shown a good correlation between the mass loss, the elemental composition and the fungal durability, confirming the possibility to predict the decay durability of the heat treated wood on the basis of its carbon content or O/C ratio. This study is an interesting preliminary stage to the development of quality control methods aimed to certify the product quality to the customers.

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Prediction of Flooring-relevant Properties Based on Colour Values of Thermally Modified Timber (TMT)

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Keywords: Colour values, bending strength, decrease in mass, hardness, intensity, heat transfer coefficient

ABSTRACT

As a result of growing quality demands from manufacturers and end-consumers of thermally modified timber (TMT), current scientific research activities are increasingly focussed on modification mechanisms and by this on the development of applicable quality control methods. Therefore, the suitability of various measures for prediction of the treatment intensity and corresponding TMT properties were investigated in the recent past, mainly focussing on deducing the resistance against fungal decay. However, for many flooring applications, especially indoors, biological durability is not the most important material property to be considered, since the performance of floorings is amongst others mainly characterized by its optical appearance, thermal behaviour and by some mechanical properties including hardness and bending strength. Consequently, the potential of colour values to predict these flooring-relevant properties was investigated within this study. Therefore beech and spruce specimens were heat treated at 180 and 220°C for various treatment durations to achieve different treatment intensities. The results show that the decrease in mass by thermal modification (dm) is a suitable measure to describe the treatment intensity both for beech and spruce. Colour values proved to be highly correlated with dm, static mechanical strength properties, surface hardness and thermal behaviour. Consequently a prediction of flooring-relevant properties of TMT by colour values appears applicable.

INTRODUCTION

Various heat treatment processes have reached a status of commercial implementation with constantly growing market shares (EUWID 2009) accompanied by growing quality demands from converters and end-consumers at the same time. So far, mainly the basic material characteristics of thermally modified timber (TMT) and the suitability of diverse wood species and materials for thermal modification were investigated in the past (e.g. Boonstra *et al.* 2006, Unsal *et al.* 2009). Meanwhile the recent scientific research work is more focussed on the impact of the heat treatment intensity on material properties and on potential ways to determine the intensity for industrial quality control utilisation (Welzbacher *et al.* 2007, González-Peña and Hale 2009, Inari *et al.* 2009). To describe the heat treatment intensity the decrease in mass by thermal modification (dm) turned out to be a suitable measure (i.e. Del Menezzi and Tomaselli 2006, Inari *et al.* 2009). It was shown exemplarily with thermally modified spruce in earlier studies (e.g. Welzbacher *et al.* 2007, 2009) that dm is significantly correlated with numerous properties of TMT, like swelling, moisture absorption, colour change, resistance against fungal attack, chemical constitution and dynamic mechanical strength properties.

Besides other methods within this previous study, the CIE L*a*b*-colour measurement proved to be a suitable tool to deduce dm and by this to predict particular target properties of spruce-TMT, e.g. resistance against fungal decay. However, especially for indoor floorings and decking the durability is not the most important target property of TMT (i.e. Brischke *et al.* 2005). In this respect mechanical strength, surface hardness and thermal properties become the decisive property of the material. In particular thermal properties of flooring materials play an important role for any interior and exterior application, especially where persons directly contact the floor with the skin, e.g. bed rooms or outdoor decking. Nevertheless, the thermal comfort is influenced not only by the surface temperature, but also by the flooring material itself. Floors may feel differently warm or cold respectively, although their temperature is the same (Waltjen 2003). In contrast to interior applications, where heat dissipation is the major problem, for outdoor flooring the focus is on extremely high surface temperatures of up to 80°C as they can occur at dark coloured decking's during the summer. When walking on such warmed-up garden paths, terrace pavements, or open air pool decking, the heat transfer from the material to the foot may lead to inconvenience or even pain. In this context wood-based materials promise higher thermal comfort compared to other flooring and decorating materials (Barreira and de Freitas 2007) since wood products are appreciated as insulating materials as they reveal low thermal conductance. Consequently it can be assumed that wood based materials may also show advantages related to the heat impact of outdoor flooring materials on human bare feet. Therefore the aim of this study was to determine flooring relevant properties (mechanical strength, surface hardness and heat transfer) for thermally modified timber and to investigate their dependence on the heat treatment intensity. Furthermore, the aptitude of colour values to act as a marker to deduce these flooring relevant properties was investigated.

EXPERIMENTAL

Heat treatments

In each case 200 axially matched stakes of 550 x 30 x 55 mm³ (long. x tang. x rad.) were cut from five different planks of Norway spruce (*Picea abies* Karst.) and European beech (*Fagus sylvatica* L.). From each species 180 stakes were submitted to various heat treatments in a drying oven at different treatment temperatures and times (Table 1).

Table 1: Heat treatment temperature and time; n=18 specimens were used for each combination.

Wood species	Treatment temperature [°C]		Treatment time [h]					
	180	220	0.0	1.5	4.0	16.0	36.0	72.0
Norway spruce	180	220	0.0	1.0	2.0	3.0	6.3	10.0
	180	220	0.0	1.5	4.0	8.0	16.0	36.0
European beech	180	220	0.0	1.0	2.0	3.0	4.0	6.0
	180	220	0.0	1.5	4.0	8.0	16.0	36.0

The stakes were tightly wrapped in aluminum foil to minimize oxidation processes. The decrease in mass (dm) during the thermal modification process was used as a measure of the heat treatment intensity. It was determined by weighing the oven-dried specimens before and after the heat treatment to the nearest 0.01 g.

*CIE L*a*b* color measurement*

Colour measurements were recorded on planed surfaces at three points per specimen with a colorimeter (Spectro-Guide Sphere Gloss, BYK-Gardner GmbH, Germany). The measurements were taken in CIE L*a*b* coordinates. A cumulated colour value based

on the addition of the lightness L^* and the chromatic coordinates of the blue-yellow axis b^* ($L + b$) was calculated and used for all correlations with material properties determined, as suggested by Brischke *et al.* (2007)

Determination of static bending strength

A three point bending test after DIN 52 186 (1978) was run with specimens of 360 x 20 x 20 mm³ on a universal testing machine Zwick Z100 to determine the bending strength.

Determination of surface hardness

The Brinell hardness was determined according to DIN EN 1534 (2000) on a universal testing machine Zwick Z100 at five points per specimen of 140 x 30 x 25 mm³.

Determination of thermal properties

Besides Bangkirai (*Shorea spp.*) and WPC-boards as reference, untreated and heat treated spruce (220°C, 3 and 10h) and beech (220°C, 2 and 6h) specimens were used. The specimens of 140 x 30 x 25 mm³ were conditioned at 80 °C in a drying oven. For the determination of the thermal behaviour a silicone pad of 1 cm³ in volume (Ø: 17 mm, h: 4.4 mm, A: 227 mm²) with a centrally embedded thermo couple was placed on the conditioned specimens. To mimic real skin contact conditions the pad was conditioned at 35 °C before measuring. The temperature increase of the silicone pad, which was covered with polystyrene foam insulating material, was then recorded over 60 s in intervals of 1 s. To obtain a contact pressure equivalent to a human load of 70 kg on two feet, which have an average contact area of 0.018 m², 1 kg was applied to the sensor pad. The heat flux density and the heat transfer coefficient (h) as a measure for the thermal behaviour were calculated according to equation 1 and 2.

$$\text{heat flux density } \dot{q} = \frac{Q}{A \cdot \Delta t} \quad \left[\frac{W}{m^2} \right] \quad (1)$$

Q = thermal energy [J], A = contact area [m²], Δt = period of time [s]

$$\text{heat transfer coefficient } h = \frac{\dot{q}}{\Delta T} \quad \left[\frac{W}{m^2 \cdot K} \right] \quad (2)$$

\dot{q} = heat flux density [W/m²], ΔT = temperature difference [K]

RESULTS AND DISCUSSION

Heat treatment intensity

With increasing treatment temperature and duration, a significantly rising decrease in mass (dm) representing the heat treatment intensity was found for spruce and beech (Figure 1), which is in line with prior studies, *e.g.* Welzbacher *et al.* (2007) and Gonzáles-Peña and Hale (2009). As expected, the influence of the treatment temperature on the treatment intensity was significantly stronger pronounced than the influence of the treatment time.

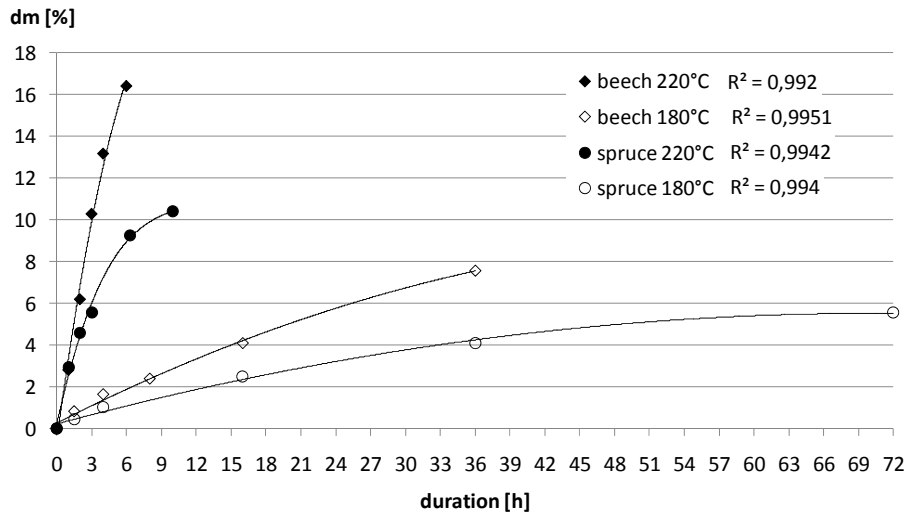


Figure 1: Correlation between decrease in mass (dm) and treatment time for different heat treatment temperatures; each dot represents the mean value of 15 specimens.

Colour measurements

An excellent correlation between $L + b$ and dm was found for all specimens, independent from the wood species used and treatment temperature applied (Figure 2). This independency of colour values from the treatment temperature in conjunction with the independency from the origin of the specimens (Brischke *et al.* 2007) points to the high potential of colour measurements as a tool to characterize the treatment intensity.

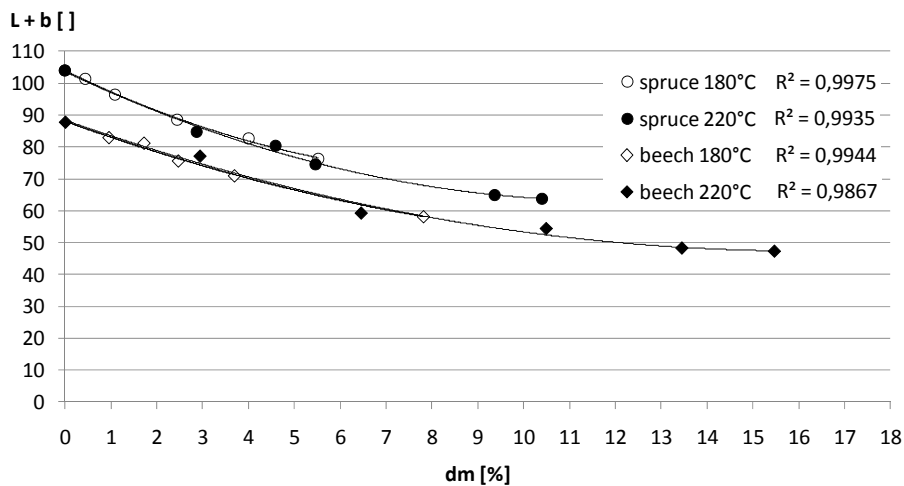


Figure 2: Correlation between the cumulated colour value $L + b$ and the decrease in mass (dm) by heat treatment at different temperatures; each dot represents the mean value of 15 specimens.

Static bending strength

The static bending strength (MOR) decreased with increasing heat treatment intensity (Figure 3). Considering the actual treatment intensity as basis for comparison, it became clear that the mechanical strength of specimens treated at lower temperatures, but prolonged durations, were more affected than the mechanical strength of specimens treated at higher temperatures, but shorter durations. This was valid for both wood species.

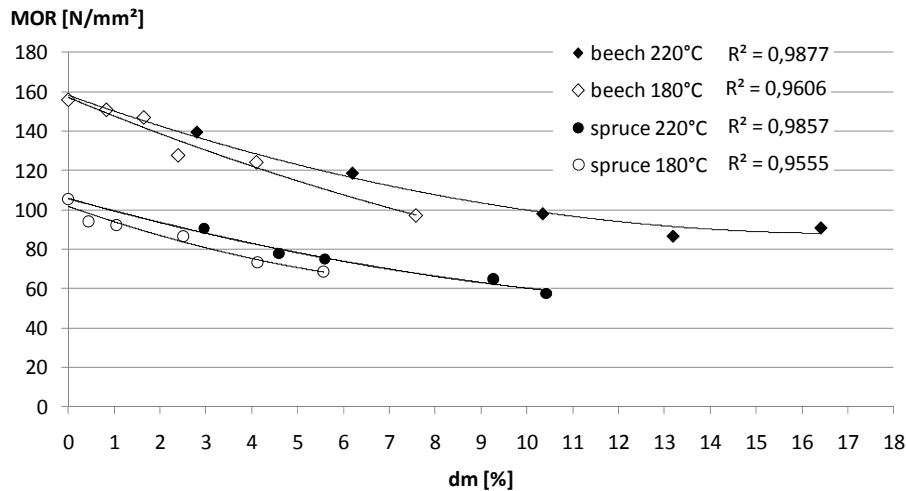


Figure 3: Relation between the static bending strength (MOR) and decrease in mass (dm) by heat treatment at different temperatures; each dot represents the mean value of 15 specimens.

Brinell hardness

A temperature independent relation of decreasing radial hardness (HB) and increasing heat treatment intensity (dm) was found (Figure 4) which is in line with previous results from Brischke *et al.* (2005). In contrast, axial hardness was not affected by heat treatments, as also stated by Jämsä and Viitaniemi (2001).

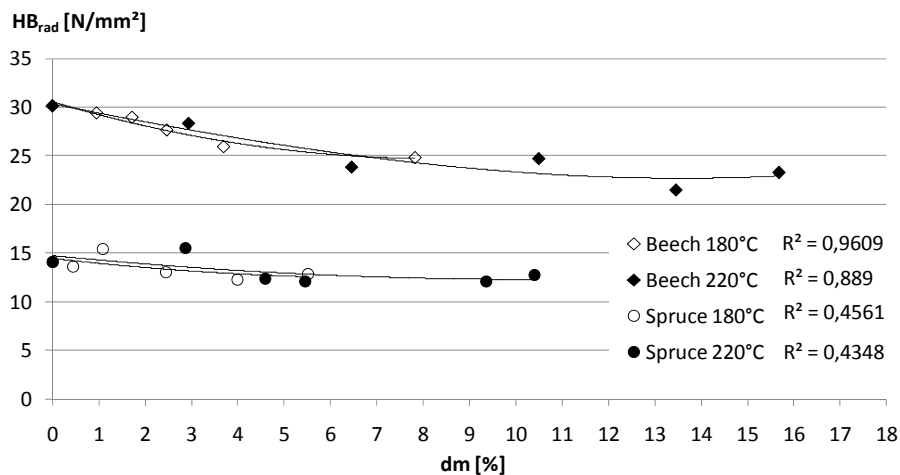


Figure 4: Relation between the radial Brinell hardness (HB_{rad}) and decrease in mass (dm); each dot represents the mean value of 15 specimens.

Thermal properties

The heat transfer coefficient (h) was related to both density and dm: With increasing dm and decreasing density h also decreased (Table 2). This is explained by the fact that the thermal effusivity of a material is among other impacts dependent on the material density (Baehr and Stephan 2004). Density itself is on the other hand affected by heat treatments and the particular heat treatment intensity (*i.e.* Del Menezzi and Tomaselli 2006). However, the heat transfer of TMT was significantly lower compared to Bangkirai and WPC that reached the limit value of 40 W/m², above which test persons experience an “inconvenient to painful” thermal sensation (Boeckmann 2010).

Table 2: Heat treatment parameter, density, decrease in mass (dm) and heat transfer coefficient (h) of the materials tested; n=10 measurements per material.

wood species	heat treatment	oven dry density [kg/m ³]	dm [%]	h [W/m ² *K]
spruce	untreated	0.43	0.0	22.4
	220°C / 3h	0.39	5.6	22.4
	220°C / 10h	0.39	10.6	20.1
beech	untreated	0.65	0.0	31.7
	220°C / 2h	0.64	6.2	31.0
	220°C / 6h	0.62	16.7	29.5
Bangkirai	untreated reference	0.84	0.0	39.9
WPC	untreated reference	1.21	0.0	49.7

Prediction of properties by colour values

Since all determined properties showed a strong dependency on the decrease in mass [MOR = f(dm), HBrad = f(dm), h = f(dm), L+b = f(dm)] correlations between the target properties (MOR, HBrad, h) and the indicator measure (L+b) were established (Figure 5).

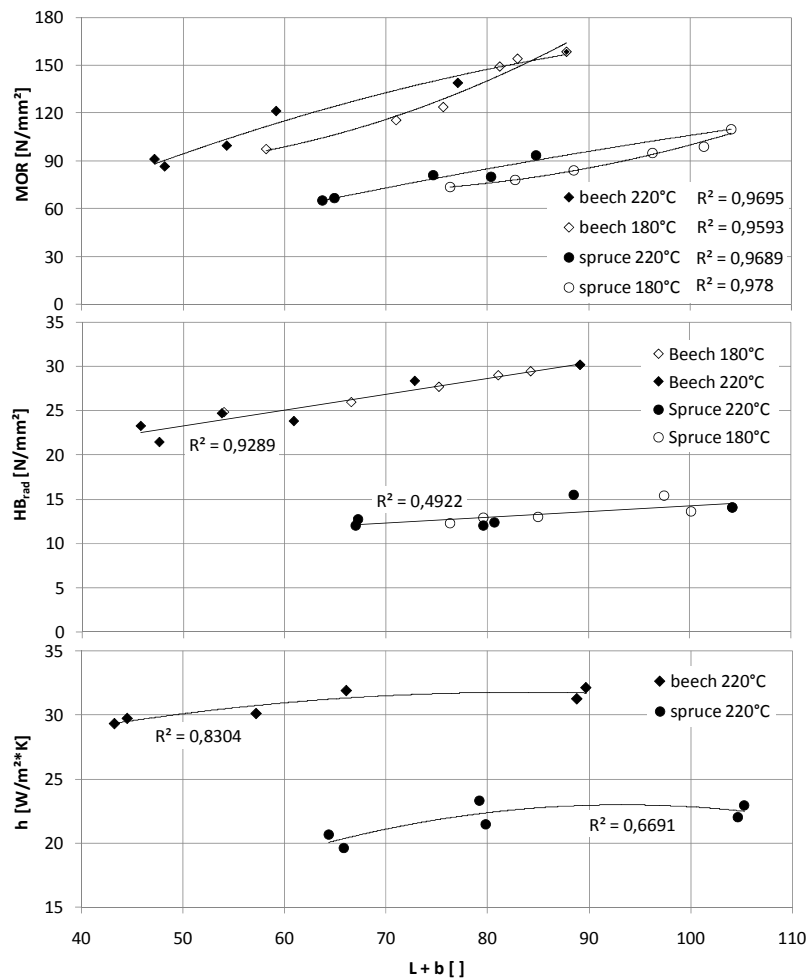


Figure 5: Correlation between colour values (L+b) and bending strength (MOR), hardness (HBrad) and heat transfer coefficient (h); each dot represents the mean of 15 specimens (5 for h-determination).

For both, spruce and beech, strong correlations were established between target and indicator measures. A temperature dependency was found for bending strength but not for radial hardness. However, the results demonstrate the aptitude of colour values to estimate the flooring relevant properties of heat treated timber at hand if the treatment temperature is known.

CONCLUSIONS

The findings underlined the suitability of the L*a*b*-colour measurements as a short term test method to predict flooring relevant properties of thermally modified timber. This was valid for both spruce and beech, which shows that the utilization of colour measurements is not limited to single wood species. However, the different correlations between colour values and heat treatment intensity of beech and spruce point to the need to establish individual correlations of predictive and target properties for all wood species and all single processes applied.

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**Session Four:
Poster Session 1**

Influence of a Prior Chemical Treatment on Properties of Thermally Modified Wood

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Keywords: chemical modification, volatiles, gas chromatography, dimension stability

ABSTRACT

Intensified demand on native dark woods is one reason for increased interest in the production of thermally modified wood. On one hand thermally modified wood is comparable to tropical hardwood in durability, dimension stability and moisture content. On the other hand it is characterized by a typical odour caused by several degradation products of wood components which are malodorous and supposed to be harmful. It was supposed that chemical pre-treatment can reduce those malodorous emissions while increased mechanical properties and dimension stability are not unfavourably affected by the chemical treatment. This study investigates the impregnation of wood specimens (*Acer spec.*) with different chemical solutions prior to thermal treatment to reduce the formation of these VOCs by restraining the improved properties of thermally modified wood. The chemicals were supposed to react with either the wood components or its degradation products. To determine the changes of the chemical composition, the samples were analysed and described by using GC/MS and FT-IR spectroscopy. Mechanical changes were identified by determining by flexural modulus of elasticity.

INTRODUCTION

Wood as renewable resource is degraded by ultraviolet radiation, weather as well as by biological influences. Thermal modification is a common way to increase resistance to fungi and microorganisms (Boonstra *et al.* 2007; Weiland and Guyonnet 2003) and dimension stability (Popper *et al.* 2005) of local woods while dark discolouration makes it an alternative to tropical hardwoods. Certainly indoor application of thermally modified wood is limited by its typical odour, which is malodorous and supposed to be harmful. This odour is caused by emission of wood degradation components like acetic acid, furfural and 5-methylfurfural (Peters *et al.* 2008). As indoor applications of thermally modified wood are rather interesting, it is necessary to elaborate ways to reduce the malodorous emissions. It is a fact that a reduction of VOCs can be achieved by solvent extraction of thermally modified wood (Peters *et al.* 2008). Also the chemical impregnation of wood prior to the thermal treatment is supposed to reduce the malodorous emissions significantly by reacting with wooden components and/or its degradation products, inhibiting the formation of these volatile compounds. To reduce odorous degradation products, defined specimens of Maple (*Acer spp.*) are pre-treated with several chemical solutions prior to thermal modification. The chosen chemicals are characterized by either reactive functional groups or a potentially buffering effect. It was supposed that those chemicals react with the wood components degradation

products such as acetic acid, furfural and 5-methylfurfural. Thermal modification is performed in a laboratory autoclave at 180°C with inert gas atmosphere. The volatiles resulting from the modification process were analyzed and described with Headspace SPME and Gas chromatography/mass spectrometry. Analyses were done in comparison with a native as well as a common thermally modified sample and the respective thermal untreated reference for each chemical used. The volatile substances were assessed in reference to their resource as well to their health and environmentally relevance. In each case the composition of volatiles is changed compared to the different reference samples. In the case of chemical treatment with urea-solution and borate-buffer a significant reduction of malodour after thermal modification can be recognized corresponding with decreased content of furfural detected. Treating wood with chemicals will also have an influence on the physical and mechanical properties. Prepared wood specimens were analyzed on variation of dimension stability, modulus of elasticity and moisture content due to thermal and chemical treatment in comparison to untreated reference samples. It was detected that the sample with the lowest noticeable odour provides also the best values for modulus of elasticity.

EXPERIMENTAL

Samples (140 mm *10 mm * 10 mm) were taken from a single wooden board (*Acer* spp.). The impregnation with chemical solutions was implemented under vacuum up to weight balance of the specimens. Re-dried samples were thermally modified in an autoclave under nitrogen atmosphere for 5 h at 180°C. Headspace Solid-Phase micro extraction (HS-SPME) was used for enrichment and further investigation of volatile emissions of wood samples by gas chromatography. Sampling was performed manually with a Supelco SPME sample holder using an 85 µm carboxen-polydimethylsiloxane coated fibre. Therefore 1 g of splints of each sample was placed into a 20 ml headspace vial, and the analyte was extracted by exposing the SPME fibre to the gaseous wood emissions at 70°C for 1h. Subsequently, the analyte-enriched fibre was thermally desorbed in the gas chromatograph injection port for. Gas chromatography/mass spectrometry analyses were performed on an Agilent Technologies HP 6890 gas chromatograph equipped with an Agilent Technologies MSD 5973. The substances were separated on an Optima5 capillary column (Macherey-Nagel) using Helium as the carrier gas. Electron impact mass spectra were recorded at 70 eV in the m/z range of 10-550. The substances were identified by analysis of the individual mass spectra and comparison with the NIST 2.0 mass spectral library or with reference standards analyzed at the same conditions as the sample material. Flexural modulus of elasticity were determined by a three-point bending test on TIRA test 28100, equipped with a load cell of a metering range of 10 kN. The test was performed on samples being conditioned under standard atmosphere. Annual rings were arranged vertically towards the application of force. The test was designed according to DIN 52186. Anti-swelling-efficiency (ASE) has been used for quantifying the dimensional stability. Measures were taken from samples being conditioned under standard atmosphere and dried at 103°C.

RESULTS AND DISCUSSION

Volatile emissions

The most noticeable reduction of the malodorous emissions was achieved by applying a 0.25 M urea solution to the specimens. Figure 1 show the SPME gas chromatograms of the urea impregnated and native samples, thermally treated and thermally non-treated.

Considerable changes occurred at native maple samples after the impregnation with 0.25 M urea solution by the formation of ethyl acetate or diethyl maleate. Otherwise, no longer remarkable signals of alkanals can be detected which are typical in emissions of native maple reference.

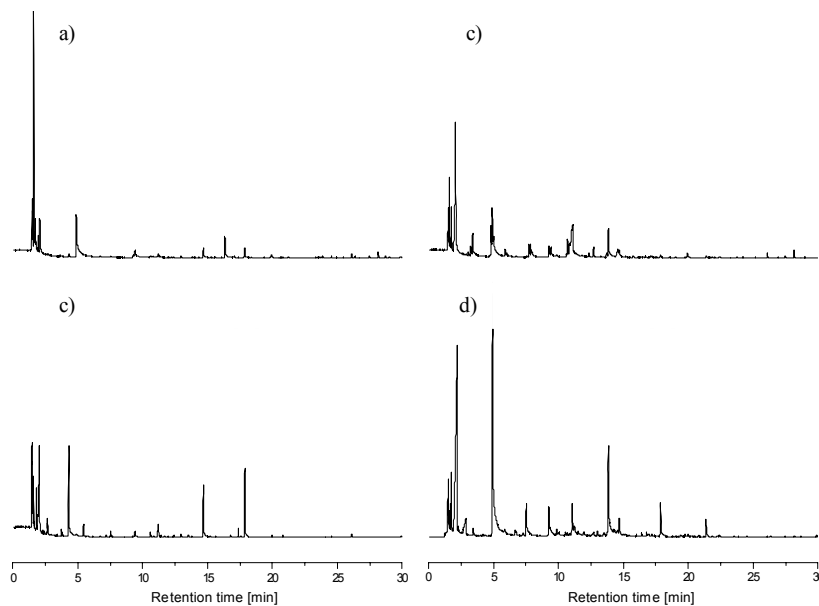


Figure 1: HS-SPME GC of maple samples a) native (impregnated with 0.25 M urea); b) thermally modified (impregnated with 0.25 M urea); c) native reference, d) thermally modified reference.

The thermal modification of urea-impregnated samples led to a further change of the chemical composition, compared to impregnated thermally non treated samples as well as compared to the native thermally treated reference. The HS-SPME-GC/MS of the urea-impregnated thermally treated sample detected the most intensive signals for ethyl acetate, furfural, urethane and pyrrole-2-aldehyde. Acetic acid, one of the main components in emissions of chemical not treated thermally modified maple, could not be found in the emissions of the urea-impregnated samples. Generally, acetic acid in thermally modified timber is known for lowering the pH and consequently for catalyzing further degradation of wood components. However, there is a much less intense signal of furfural after pre-treatment with urea compared to the native thermally modified samples. Possibly this allowed the reduction of the malodorous odour.

Flexural modulus of elasticity

The chemical constitution of materials is strongly linked with structural, physical, and mechanical properties. Impregnating wood with a 0.25 M urea solution has evidently caused changes in the chemical constitution, initialising a degradation of the hemicellulose as was found out by performing HS-SPME-GC/MS. This initialized degradation has affected the strength properties of the samples as shown in figure 2. Compared to the flexural modulus of elasticity of native thermally non modified timber, the values of urea impregnated samples decreased. However, the results of the HS-SPME-GC/MS of urea-impregnated thermally modified samples indicate a reduced degradation compared to the native thermally modified samples. Again, there is an analogy with the flexural modulus of elasticity (Figure 2). The values of the flexural modulus of elasticity increased significantly after a pre-treatment of the samples with a 0.25 M urea solution compared to native thermally modified samples.

Dimensional stability

In general, thermal modification of wood obtains an increased dimensional stability (maple: 23.42 %). The impregnation of samples with a 0.25 M urea solution prior to thermal modification has even gained a dimensional stability of 33.39 % compared to the native thermally non modified samples.

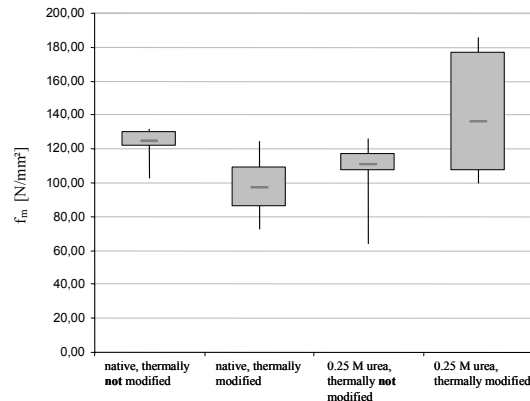


Figure 2: Flexural modulus of elasticity f_m of different maple samples

CONCLUSIONS

Generally, thermal modification leads to the formation of acetic acid, furfural and 5-methylfurfural, which cause malodorous and harmful emissions. The impregnation of maple with a 0.25 M urea solution prior to thermal modification changes the chemical composition and reactions of the wood before and during thermal modification. Reducing the degradation of the wood components, this does not only provide a reduction of the malodorous odour of thermally modified wood, but also gains an increased flexural modulus of elasticity as well as an increased dimensional stability, compared to the properties of native, thermally modified maple.

ACKNOWLEDGEMENTS

The authors are grateful to Deutsche Forschungsgemeinschaft for financial support.

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Colour Differences in Thermally Modified Wood in Dependence of the Distance from the External Surface and the Modification Parameters

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Keywords: colour, colour differences, thermally modified wood

ABSTRACT

Spruce (*Picea abies* Karst.) and ash (*Fraxinus excelsior* L.) were thermally modified in an inert gas atmosphere by different temperatures and durations. The surface of each sample was milled stepwise at approximately 1 mm to at least 8 mm. At each obtained surface the colour was measured using the CIE $L^*a^*b^*$ system and compared with the colour of the external surface. Thus colour differences between the generated interior and the external surface could be evaluated.

INTRODUCTION

The thermal modification causes colour changes in the wood. In dependence of the duration of the modification process the wood becomes more or less dark (Bekhta and Niemz 2003). Concerning the decorative value of thermally modified wood the colour is a determining factor. In general the production of interior or other structural elements requires a milling of the external layers of the wood. In such a case the colour of the wood should be the same independent of the milled or planed thickness. In order to investigate colour differences inside of the thermally modified wood colour measurements were carried out in different distances from the external surface of the wood.

EXPERIMENTAL

The investigations were carried out with wood modified at different temperatures and durations. Specimens (100 mm length x 100 mm width x 20 mm thickness) of the wood species ash (*Fraxinus excelsior* L.) and spruce (*Picea abies* Karst.) were thermally modified in an inert gas atmosphere. As temperatures 180°C and 200°C were used. The duration of the modification process was varied with 1 h, 4 h, 6 h, 8 h and 12 h. The surface of each sample was milled and grinded stepwise at approximately 1 mm to at least 8 mm. After each milling step colour measurements were carried out at the generated surfaces. Thus the colour inside of the modified wood could be evaluated in comparison to the original external colour. The colour was described using the CIE $L^*a^*b^*$ system, where the three parameters L^* , a^* and b^* corresponds to the coordinates in the three-dimensional colour space. L^* represents the position of the black – white axis, a^* represents the position of the red – green axis and b^* represents the position of the yellow – blue axis. Colour differences are expressed with the

parameter ΔE^*_{ab} , which is defined as the Euclidian distance between two points in the three-dimensional colour space (Eqn. 1, DIN 5033 and DIN 6174).

$$\Delta E^*_{ab} = ((L^*_s - L^*_r)^2 + (a^*_s - a^*_r)^2 + (b^*_s - b^*_r)^2)^{1/2} \quad (1)$$

A reference value (index r) is always necessary to calculate ΔE^*_{ab} . In general a value of ΔE^*_{ab} of 1 to 2 is described as a noticeable colour difference, but the texture of the natural material wood often leads to differences in this range. A value of 5 or higher is in general evaluated as another colour.

RESULTS AND DISCUSSION

The figures 1 and 2 show the results for modified ash and spruce wood. As reference values for the calculation of the colour difference ΔE^*_{ab} the colour parameters of the external surface were used.

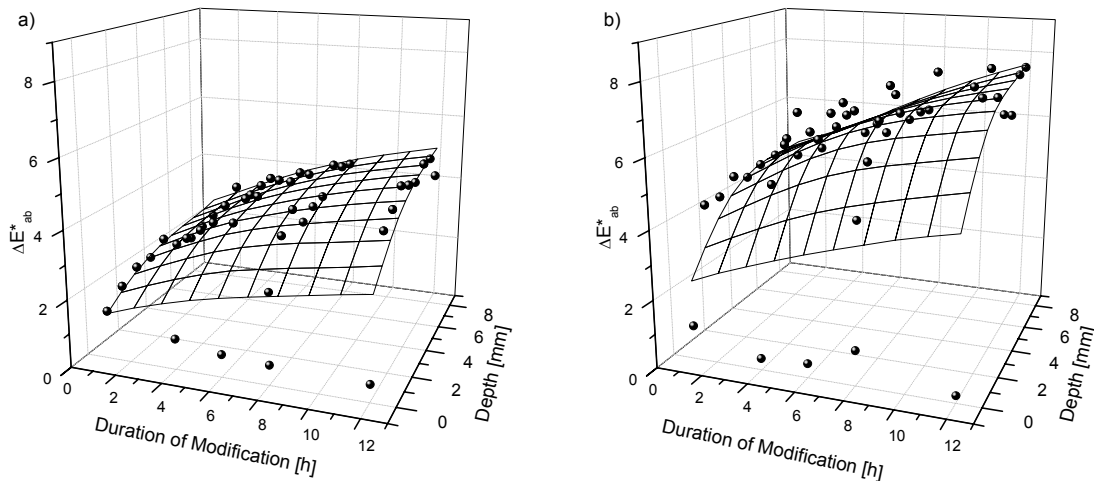


Figure 1: Colour differences of ash modified with a) 180°C and b) 200°C, referred to the external surface

The figures clearly show a dependence of the colour from the depth of the measurement. With increasing distance from the surface the colour difference increases. The wood becomes lighter. The colour differences are more obvious when the wood is modified with a temperature of 200°C. Also the increasing duration of the modification leads to a more obvious colour difference. Thereby the values for ΔE^*_{ab} are in a range where the internal colour have to evaluated as another colour. If as reference values the colour parameters of the first milled surface, measured at approximately 1 mm distance from the external surface are used, the following colour differences, shown in the figures 3 and 4, occurs. The reference of the internal colour parameters to the first processed surface results in clearly less colour differences. Colour differences are existing anymore, but the level is clearly reduced. There is a dependence of the colour of the depth and the duration of the modification observable. This dependence is more obvious for spruce. Regarding ash the colour values are quite homogenously. These colour differences are in the range of natural wood.

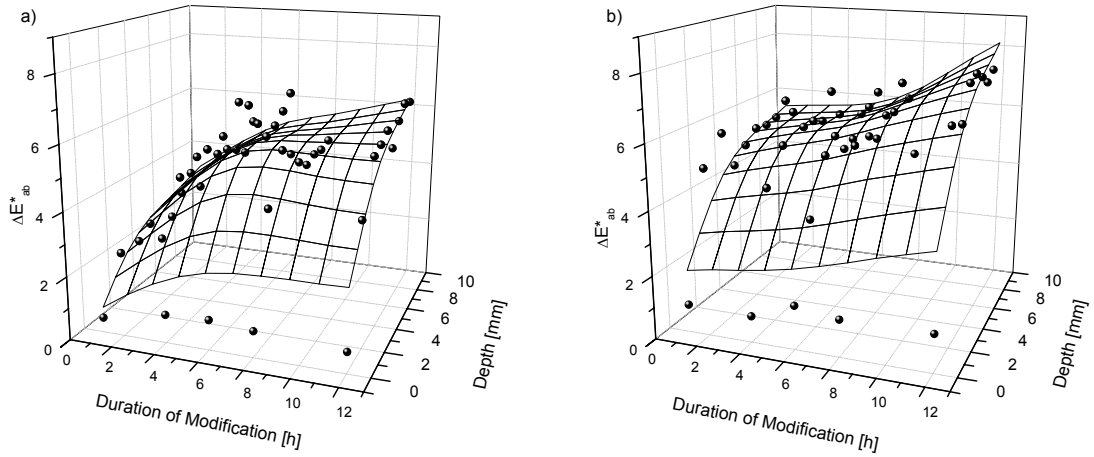


Figure 2: Colour differences of spruce modified with a) 180°C and b) 200°C, referred to the external surface

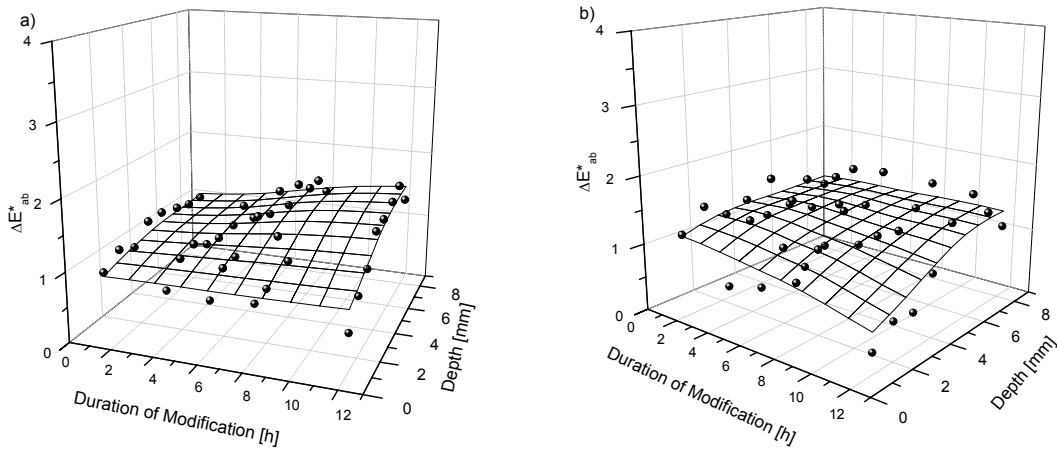


Figure 3: Colour differences of ash modified with a) 180°C and b) 200°C, referred to the surface at 1 mm distance from the surface

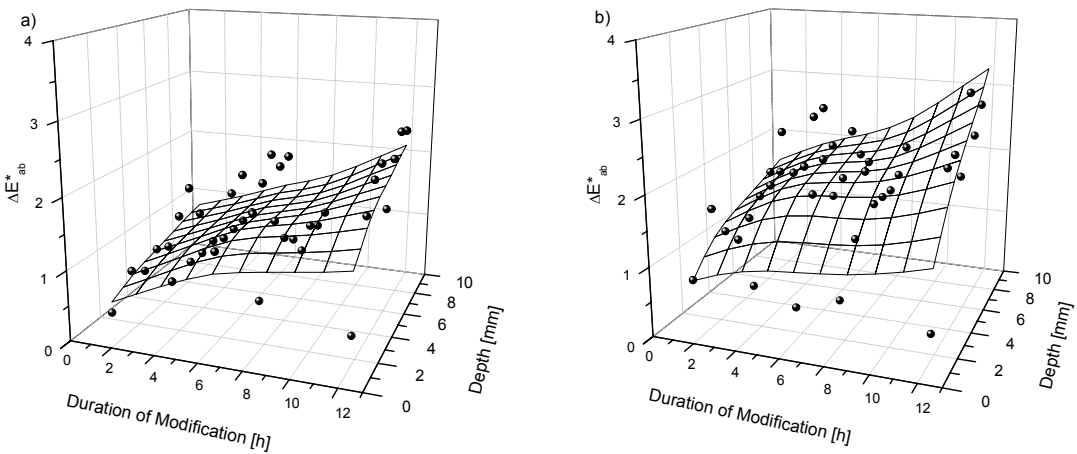


Figure 4: Colour differences of spruce modified with a) 180°C and b) 200°C, referred to the surface at 1 mm distance from the surface

CONCLUSIONS

The thermal modification causes colour changes in the wood, which are not uniformly within the whole modified wood. There are colour differences between the external surface and surfaces inside of the wood. Thereby the external surface is darker than the inside of the wood. These differences are higher with higher duration and temperature of the modification process. The biggest step to another colour seems to occur within the first millimetre of the modified wood. If a small layer of approximately 1 mm is milled, the colour differences are clearly reduced. Regarding spruce as one investigated species some colour differences are between 2 and 3. These values are evaluated as an observable colour difference. But the other differences are in the range of a natural, alive, inhomogeneous surface of wood. For the processing of thermally modified wood the results mean that the surface should be milled if other inner surfaces also should be seen in the end product.

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Revaluation of European Hardwood Species by Combined Modification, Compression and Shaping Processes

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Keywords: Compressed wood, hardness, furfuryl alcohol, spring-back-effect

ABSTRACT

The aim of a project at the TU Dresden is the revaluation of European hardwood species by a combined modification, compressing and shaping process. Therefore wood samples of beech were impregnated with a two component solution consisting of furfuryl alcohol and anhydrites of carbon acids. It undertakes the tasks of plasticization as well as the fixation of the shape after the densification and shaping process. Compressing of these impregnated samples at approx. 30 % and following curing in a heating press resulted in a clearly increase of the hardness. The well known spring-back-effect, known from the utilisation of common softeners like water or ammonia, are prevented by the in-situ polymerisation of the furfuryl alcohol to furan resins resulting in the fixation.

INTRODUCTION

Special demands can often be conformed by choosing a wood species that is designed for enduring high stress or other special tasks. Thereby the tropical and subtropical wood species, whose population are often endangered by overexploitation, provide the largest multiplicity of species. One especially extreme example is demonstrated by high-quality Asian ebony (*Diospyros ebenum* J.Koenig, *Diospyros melanoxylon* Bakh.), which is in fact eradicated except of remainders in Myanmar and Sri Lanka. Ebony features a very high material hardness and dimensional stability. A similar situation arises from African Blackwood (*Dalbergia melanoxylon* Guill. et Perr.), although this is a less acute situation. Thus it can be foreseen by now that substitution materials will be needed presently for Ebony and African Blackwood. The aim of a project at the TU Dresden is the revaluation of European hardwood species by a combined modification, compressing and shaping process. Thereby the shaping process can conform different tasks. It can be used for increasing the density of a plane wood sample. In that case the densification is regarded as plastic deformation. Other tasks may be a non-cutting shaping with nearly constant density or a combination of both processes. The shaping process occurs near-net-shape, *i.e.* there are no fundamental following process steps necessary concerning the shaping. Besides the shaping the strengths, especially the hardness, are enhanced as result of the enhanced density and the dimensional stability of European hardwood species are improved and in that way revaluated. This procedure occurs by a combined process, where the process steps plasticization, densification, shaping and fixation of the shape occurs in one operation, *e.g.* in a heating press.

EXPERIMENTAL

Wood samples of beech were impregnated with a two component solution consisting of furfuryl alcohol and anhydrites of carbon acids. It undertakes the tasks of plasticization

as well as the fixation of the shape after the densification and shaping process. The fixation of the shape is reached as result of a temperature induced acid catalytic polymerisation of furfuryl alcohol. Thereby covalent bonds to the wood substance are linked (Nordstierna *et al.* 2008). Different weight percentage gains (WPGs) were set in the wood by ethanol thinned furfuryl alcohol (Hadi *et al.* 2005). The impregnation was carried out in an autoclave by a vacuum and pressure stage (Lande *et al.* 2004, Venas and Felby 2009). After vaporisation of the ethanol by a low temperature drying the impregnated wood samples were densified at temperatures of 120°C and 140°C in radial direction. Densification rates of 30% were realised. Stress-strain-curves were regarded for characterizing the compression behaviour. The samples were remained in the closed press for 30 min. Then they were cured in a laboratory oven at 103°C for 24 h. The density and the hardness were determined. Subsequently a cyclic water storage and drying process was carried out due to determine the spring back.

RESULTS AND DISCUSSION

The impregnation with furfuryl alcohol results in a clearly plasticization of the wood (Fig. 1). In figure 1 stress-strain-curves of native and furfuryl alcohol treated wood are shown comparatively with a compression rate of 30%. The needed deformation forces are reduced clearly compared to the native wood. The Youngs Modulus is reduced by 50%. Concentrations of the furfuryl alcohol of more than 25% in the impregnation solution do not lead to an important improvement of the plasticization.

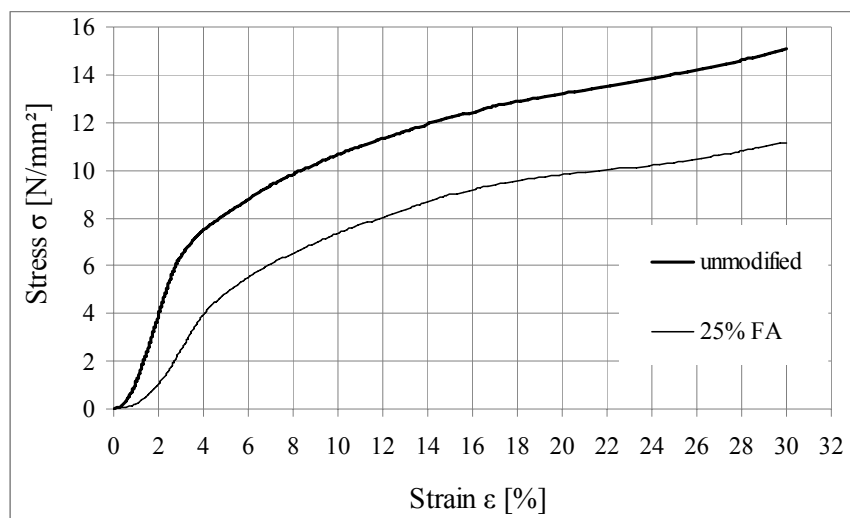


Figure 1: Stress-Strain-Curves by densification of unmodified and FA impregnated beech samples (densification rate: 30%)

Due to the process a considerable increase of the density is regarded. Figure 2 shows the densities, that are reached with a densification rate of 30%, in dependence of the WPGs.

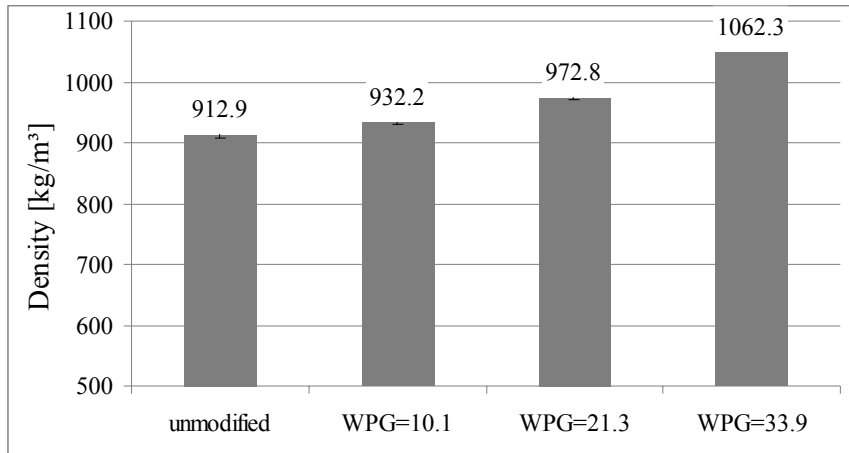


Figure 2: Resulting density after densification and curing (densification rate: 30%)

Compressing of the impregnated samples at about approx. 30 % and following curing in a heating press resulted in a clearly increase of the hardness as shown in Figure 3. With increasing WPG the hardness is increased considerably.

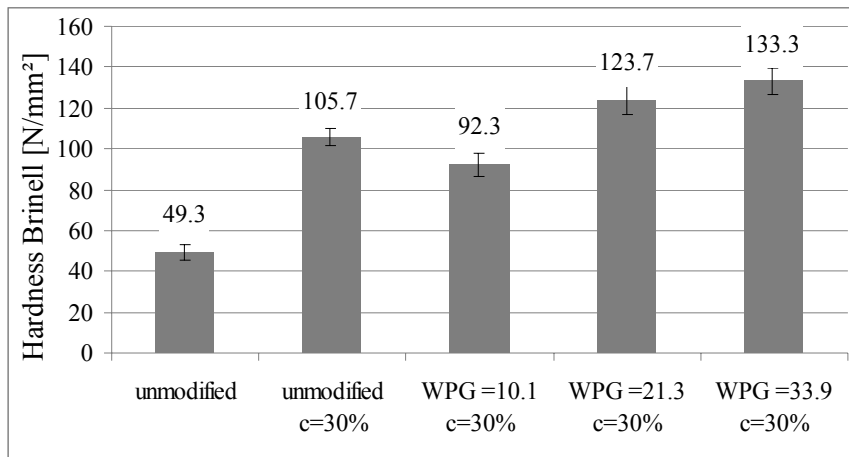


Figure 3: Hardness of FA modified and densified wood in dependence of WPG (densification rate: 30%) compared with unmodified beech

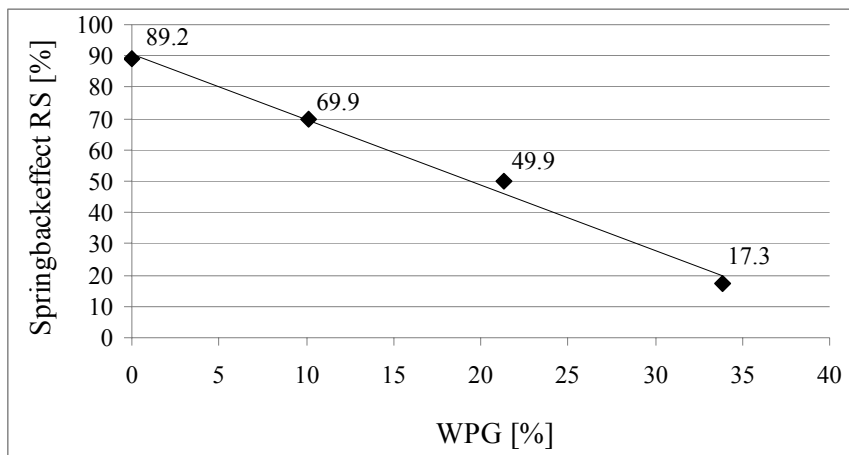


Figure 4: Spring back effect of FA modified and densified beech wood samples after last drying-wetting-cycle

In order to evaluate the spring back effect and the dimensional stability the samples were exposed to a drying-wetting-cycle for 3 times. After the third water storage cycle the remained spring back was measured as shown in Figure 4. With increasing WPG the spring back is clearly reduced. The dimensional stability of the modified and densified wood also clearly increase as shown in Figure 5. That is a result of the fixation of the compressed state due to the furan resin.

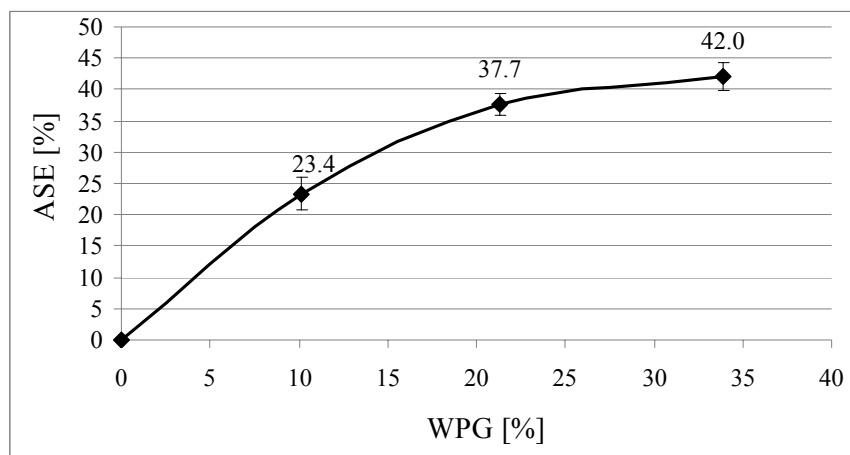


Figure 5: ASE of FA modified and densified beech wood samples after last drying-wetting-cycle

CONCLUSIONS

Samples of beech impregnated with furfuryl alcohol and anhydrides of carbon acids were densified and cured. Furfuryl alcohol undertakes the tasks of plasticization as well as the fixation of the shape after the densification and shaping process. Compressing of these impregnated samples at about approx. 30 % and following curing in a heating press resulted in a clearly increase of the hardness. The well known spring-back-effect, known from the utilisation of common softeners like water or ammonia, are prevented by the in-situ polymerisation of the furfuryl alcohol to furan resins resulting in the fixation.

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Mechanical and Interfacial Adhesion Properties of Acetylated Wood Fibre Reinforced Polypropylene Composites

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Keywords: Acetylation of wood fibres, mechanical properties, interfacial adhesion

ABSTRACT

Influences of the wood fibre acetylation and the compatibilizer MAPP on interfacial adhesion and mechanical properties of the wood plastic composites (WPCs) were studied in this research. The wood fibres were acetylated with acetic anhydride and mixed with MAPP and polypropylene (PP) and the mixture was moulded in a hot press. Test samples were prepared to determine the mechanical properties of the WPCs. Interfacial adhesions between the matrix polymer PP and the acetylated fibres were studied with a SEM. Results showed that the mechanical strengths were reduced due to the acetylation. However, application of the MAPP increased slightly those properties; especially in the non-acetylated WPCs. Scanning electron microscopy showed improved interfacial bonding between the PP and the acetylated fibres. It was also revealed that majority of the failures occurred in the fibres not in the interfaces between the matrix polymer and the fibres.

INTRODUCTION

Polarity of the lignocellulosic fillers prevents the interfacial bonding between the matrix polymer and the fillers. The compatibilizers are used to improve the adhesion (Chowdhury and Wolcott 2007). The compatibilizers bear both polar and non-polar ends, which provide capability of linkages between the polar lignocellulosic fillers and the non-polar matrix polymers. Maleic anhydride grafted polypropylene (MAPP) is a polyolefin which performs as a compatibilizer and it binds the non-polar lignocellulosic fillers to the matrix polymer. Addition of the MAPP and its influences were studied by many authors (Arbelaiz *et al.* 2005). Those reports indicate that the MAPP improves the physical and mechanical properties of the WPCs. Hydroxyl groups on the lignocellulosic fillers are responsible for the prevention in the interfacial adhesions. Different techniques are used to improve the adhesions; such as chemical modification of the fibre surfaces (Dominkovics *et al.* 2007, Demir *et al.* 2006, Tserki *et al.* 2005); application of the compatibilizers (Demir *et al.* 2006). The main part of the WPCs contains the lignocellulosic fillers bearing the hydroxyl groups, which are responsible for hydrophilicity of the WPCs and perform the most important roles in absorption of the water and the moisture. Penetration of the water molecules through the micro-gaps in the interfaces between the matrix polymer and the fillers affects the physical and the mechanical properties of the WPCs (Agarwal and Broutman 1990). Alteration of the chemistry of the lignocellulosic fillers from hydrophilic to hydrophobic might affect these properties. Changing polarity of the fillers might also affect the interfacial bonding. Acetylation is known as a chemical modification technique that alters the chemistry and the hydrophilicity of the wood fibres. According to the reports, the water

and the moisture absorption of the lignocellulosic materials are decreased due to the acetylation and they become hydrophobic (Mohebbi and Hadjihassani 2008). The current research concerns the acetylation of the wood fibres to alter their chemistry to improve interfacial adhesion as a substitution of the compatibilizer MAPP to enhance the physical as well as the mechanical properties of the WPCs.

EXPERIMENTAL

The wood fibres were oven dried prior to the acetylation. Reaction of the acetylation was carried out in a stainless steel reactor at 120°C to achieve weight percent gains (WPGs) of 4.5, 7.5 and 17.68%. Acetylated and non-acetylated wood fibres (60% w/w) were mixed with the matrix polypropylene (PP) (38% w/w) and compatibilizer MAPP (2% w/w) in a Brabender Plasticorder with at temperature of 180°C. The mixing process was 8min for all treatments. Afterwards, the mixture was moulded at 180°C with a hot press. The mould size was 150×150×2mm and target density of the WPCs was 1g/cm³. Strengths of bending, tensile and impact were tested according ASTM D-7031-04, D-638-03 and D-256-04, respectively. Failures were studied on IZOD test samples with a scanning electron microscope to study the interfacial bonding between the fibres and the matrix polymer PP.

RESULTS AND DISCUSSION

Bending tests showed that MOE and MOR were reduced due to the acetylation; however, application of the MAPP increased both moduli in the WPCs (Figs. 1 & 2). Application of the compatibilizer was more effective in the acetylated WPCs than that of the non-acetylated one. The results indicated that the compatibilizer performed better role than the acetylation. The modulus of rupture is depended on the interfacial bonding as well as the properties of the sole fibres and the matrix polymer in the composites.

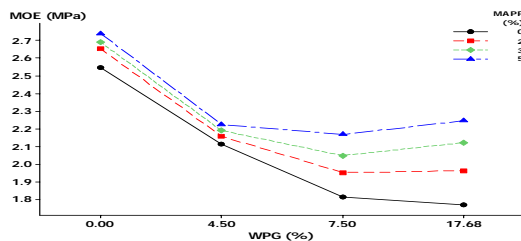


Figure 1: Interaction between acetylation and MAPP on MOE of WPCs

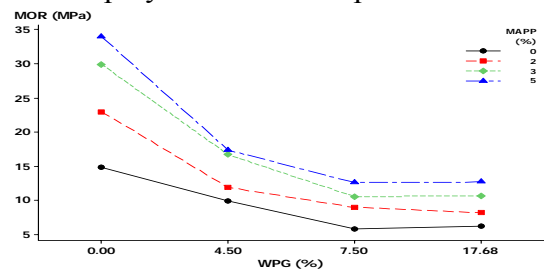


Figure 2: Interaction between acetylation and MAPP on MOR of WPCs

According to the results, the tensile strength was also reduced due to the acetylation; however it was increased as the percentage of the MAPP increases (Fig. 3). It was revealed that any increase of the tensile strength due to the MAPP was more prominent in the untreated composites than that of the acetylated WPCs. Any reduction in this property might be related to loss in the strength of the sole fibres due to the acetylation; while the MAPP could improve the bonding between the interfaces of the constituents. The fibre acetylation reduced the impact load resistance. However, application of the MAPP caused considerable increase in this property. Influence of the MAPP increase on the impact load resistance was much higher in the non-acetylated WPCs than that of the acetylated one (Fig. 4). The impact load resistance depends on the properties of the sole fibres as well as the matrix polymer and their interfacial bonding. It is probable that the strength of the single fibre was reduced due to the acetylation. The electron microscopy

showed that lack of the MAPP caused improper adhesions between the fibres and the matrix polymer PP in the WPCs with any compatibilizer. The fibres were mostly pulled off due to the poor adhesions (Fig. 5a). There were micro-spaces between the fibres and the matrix polymer PP. Application of the compatibilizer improved the adhesion properties by reducing the micro-gaps in the interfaces (Fig. 5b). The proper bonds between the fibres and the compatibilizer caused the impact failures to be appeared in the fibres not in the interfaces as seen in the WPCs with no compatibilizer.

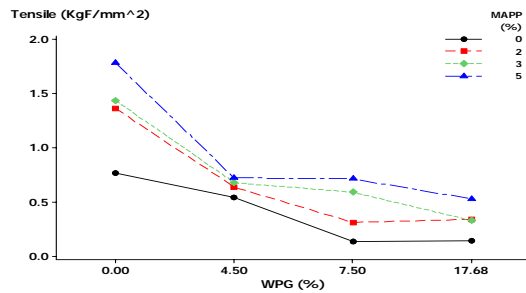


Figure 3: Interaction between acetylation and MAPP on tensile strength of WPCs

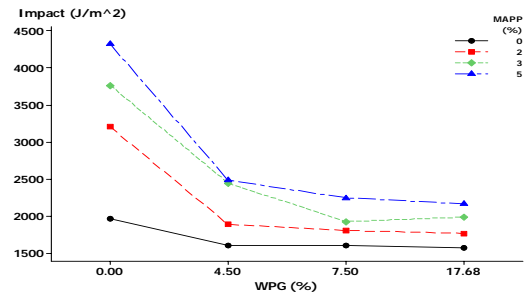
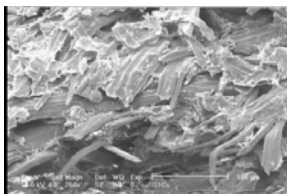
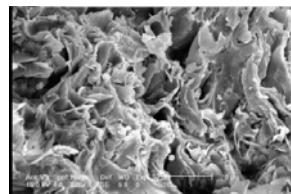


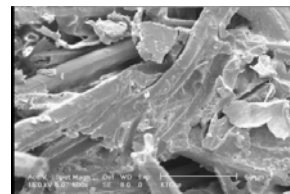
Figure 4: Interaction between acetylation and MAPP on Impact of WPCs



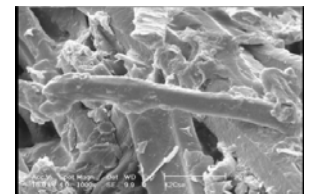
a) WPG 0%- MAPP 0%



b) WPG 0%- MAPP 2%



c) WPG 7.5%- MAPP 0%



d) WPG 7.5%- MAPP 2%

Figure 5: SEM micrographs of failures on acetylated and non-acetylated WPCs

The scanning electron microscopy of the acetylated WPCs with no MAPP showed that the interfacial bonding was improved due to the acetylation (Figs 5c). The lesser the amounts of the micro-gaps as well as the better fibre surface coverage by the PP were seen in the acetylated composites. The acetylation reduced fibre's pulling off. The proper interfacial bonding as well as the better coverage of the acetylated fibres were observed in the acetylated WPCs included the MAPP (Figs 5c). The failures were mostly appeared on the fibres. Number of the micro-gaps was less in the acetylated WPCs in which the MAPP was applied before. The SEM revealed that the acetylation improves the interfacial bonding in the composites. The interfacial adhesion properties as well as the strength properties of the sole fibres and the matrix polymer strongly affect the strengths of the wood polymer composites (Borysiak and Doczekalska 2006). Any reduction in the strength of the sole fibres due to the acetylation could decrease the strength of the WPCs. As it was determined here; the acetylated composites showed lesser strengths than that of the non-acetylated one. Also the electron microscopy revealed improved interfacial properties as well as reduction of the micro-spaces in the composite structure. As it was seen in the SEM micrographs, the impact failures were appeared mostly in the acetylated fibres; while the interfacial adhesions were still intact after application of the mechanical loads. Here, it could be expressed that the fibres were affected by the acetylation. The reports indicate that the MOE and the MOR are depended on the properties of the constituents in the wood plastic composites (Tajvidi 2005) as well as the adhesion properties between the lignocellulosic fillers and the matrix polymers (Lu 2003). The compatibilizers are normally used to improve these

properties in the composites. The electron microscopy revealed that the acetylation could improve the adhesion between the fibres and the matrix polymer; however, the strength properties were reduced due to the acetylation. Regarding the improved interfacial adhesion properties in the acetylated wood polymer composites, it is likely that any reduction in the strength properties of the acetylated fibres is the main reason for the loss of the strengths. Similar result was reported for the acetylated wood based composites (Mohebbi *et al.* 2009). Reports indicate that improvement of the interfacial adhesion between the matrix polymer and the lignocellulosic fillers affects the moduli of the elasticity and the rupture in the WPCs (Stark and Rowlands 2003, Rowell *et al.*, 2000). The MAPP improves the interfacial bonds by reacting with the hydroxyl groups of the lignocellulosic fillers. Formation of the hydrogen bonds with the MAPP and the lignocellulosic fillers in one side, and the covalent bonds with the matrix polymer in another side (Lu 2003) are the main reasons for increase of the strengths due to the application of the compatibilizer.

CONCLUSIONS

Following results were withdrawn from this research work: a) the acetylation reduced the strength properties in the wood polymer composites; also, the strength reduction is directly related to the increase of the weight gains; b) application of the MAPP increased the strengths; c) acetylation improved the adhesion properties of the WPCs. Consequently, the micro-gaps were reduced in interfaces between the fibres and the matrix polymer.

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Decay Resistance of Sapwood and Heartwood of Thermally Modified Scots Pine and Norway Spruce

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Keywords: Decay resistance, heartwood, Norway spruce, sapwood, Scots pine, thermal modification

INTRODUCTION

According to EN 335-1 (2006), the use classes 3.2 and 4 are the situations, where wood is exposed to high humidity or water for long periods and the decay risk exists. In these situations, also natural durability of untreated wood is needed. The classifying of the natural durability of wood is presented in the EN 350-2 (1994). The accelerated laboratory tests are the first steps to evaluate the potential decay resistance of new materials.

Thermal modification changes the chemical composition of wood and through that also the physical and biological properties are changed. During the thermal modification the colour of wood darkens, the dimensional stability enhances, equilibrium moisture content reduces and the biological durability increases. On the other hand, as a result of thermal modification, the wood becomes more brittle and bending and tension strength decrease in relation to the level of heat-treatment.

The biological durability of thermally modified wood has been widely studied. Viitanen *et al.* (1994) reported that the decay resistance to brown rot fungus *Coniophora puteana* according to EN-113 and soft rot fungi according to prENV807 in thermally modified spruce was significantly improved, depending on the level of the thermal modification. Hakkou *et al.* (2006) also found an important correlation between the biological durability and temperature of thermal modification. The improved fungal durability of thermally modified wood has been reported as well in many other publications (Viitaniemi and Jämsä 1996, Sailer *et al.* 2000, Tjeerdsma *et al.* 2000, Kamdem *et al.* 2002, Gosselink *et al.* 2004, Welzbacher and Rapp 2005, Jones *et al.* 2006, Mburu *et al.* 2006).

It has long been known that the chemical composition and physical properties of heartwood are different from those of the sapwood within many wood species. In our earlier study on water absorption of thermally modified Norway spruce and Scots pine, significant differences between sapwood and heartwood were detected (Metsä-Kortelainen *et al.* 2006). The aim of this study was to determine the differences in decay resistance and natural durability of sapwood and heartwood of thermally modified spruce and pine.

EXPERIMENTAL

In this study, the effects of thermal modification at four different temperatures 170°C, 190°C, 210°C and 230°C on resistance against soft- and brown-rot fungi of sapwood

and heartwood of Scots pine (*Pinus sylvestris*) and Norway spruce (*Picea abies*) were investigated using laboratory test methods. The wood materials were thermally modified using ThermoWood® method at VTT. Natural durability against the soft-rot microfungi was determined according to CEN/TS 15083-2 (2005) by measuring the mass loss and modulus of elasticity (MOE) loss after an incubation period of 32 weeks. Test material was also exposed to brown-rot fungi *Coniophora puteana* and *Poria placenta* essentially according to a mini-decay test (Bravery 1979) using two exposure periods (6 and 10 weeks) and the results were classified into the durability classes according to CEN/TS 15083-1 (2005). The results were compared with results from untreated pine and spruce samples. A detailed description of the thermal modification method and the fungal durability testing procedures are reported in other publications (Metsä-Kortelainen *et al.* 2006, Metsä-Kortelainen and Viitanen 2009).

RESULTS AND DISCUSSION

Average mass losses and MOE loss after soft and brown rot tests are presented in the Table 1. Durability classes (DC) according to CEN/TS 15083-2 (2005) and CEN/TS 15083-1 (2005) of the thermally modified wood materials are shown in the Figures 1-4.

Table 1: Average mass losses and MOE loss after decay tests.

		Soft rot		Coniophora puteana, 6 weeks	Poria placenta, 6 weeks	Coniophora puteana, 10 weeks	Poria placenta, 10 weeks
		Mass loss [%]	MOE loss [%]	Mass loss [%]	Mass loss [%]	Mass loss [%]	Mass loss [%]
Spruce, sapwood	Untreated	20,6	71,8	17,4	22,3	32,2	32,5
	170°C	18,5	71,2	15,7	18,8	28,9	28,2
	190°C	13,5	59,2	8,8	18,1	18,6	17,5
	210°C	8,2	36,1	0,2	0,0	4,5	18,8
	230°C	2,8	6,7	0,0	0,7	0,0	1,0
Spruce, heartwood	Untreated	19,0	69,6	18,6	25,0	35,2	28,9
	170°C	15,3	64,2	12,9	17,9	23,8	29,2
	190°C	11,8	52,8	7,9	17,1	19,2	24,4
	210°C	7,3	34,3	0,5	6,5	1,0	19,6
	230°C	2,8	10,2	0,0	0,8	0,0	3,6
Pine, sapwood	Untreated	20,7	69,1	16,8	27,0	33,6	31,7
	170°C	18,8	68,2	16,9	21,9	24,9	27,2
	190°C	16,2	65,5	10,5	17,2	19,1	23,1
	210°C	8,7	39,4	2,8	8,8	2,3	7,9
	230°C	5,0	18,0	0,0	0,0	0,0	1,7
Pine, heartwood	Untreated	14,9	53,9	13,8	17,6	32,8	23,8
	170°C	13,1	53,5	12,5	15,3	21,7	20,7
	190°C	9,7	44,0	8,1	12,7	16,1	19,9
	210°C	6,5	24,1	0,0	8,2	2,4	6,6
	230°C	2,7	5,8	0,0	0,0	0,0	0,1

On average, the soft-rot and brown-rot tests gave quite similar results. However, the brown-rot test gave slightly better durability classes than the soft-rot test depending on the wood material and the fungus. According to mass losses and MOE loss in decay tests, the heartwood of Scots pine was more durable against decay organisms than the

sapwood of Scots pine and the sapwood or heartwood of Norway spruce of the untreated materials. The differences between sapwood and heartwood were more significant within pine than within spruce material. The thermal modification significantly increased the decay resistance of all pine and spruce samples. The higher the thermal modification temperature, the better biological durability. *Poria placenta* fungus was more aggressive than *Coniophora puteana* against thermally modified wood, but after 10 weeks' exposure *Coniophora puteana* caused same or even higher mass losses in untreated wood than *Poria placenta*. The exposure time also significantly affected the mass losses and decay resistance. After 6 weeks' exposure the mass losses of different wood material were clearly smaller than that after a longer incubation time.

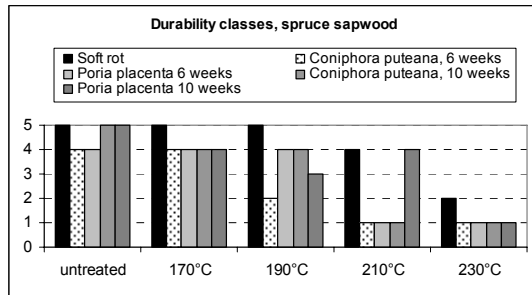


Figure 1: DC, spruce sapwood.

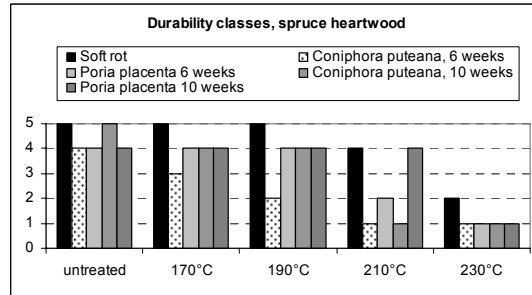


Figure 2: DC, spruce heartwood.

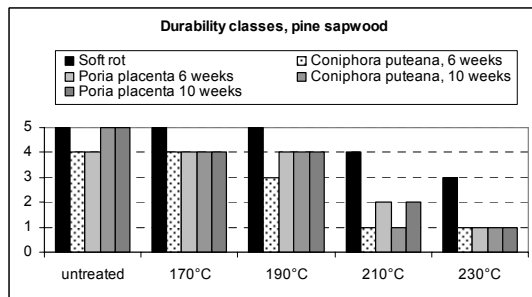


Figure 3: DC, pine sapwood.

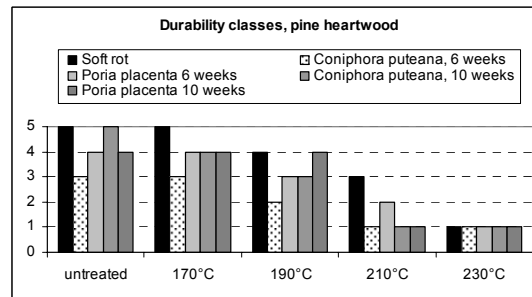


Figure 4: DC, pine heartwood.

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Densified Wood in 2- and 3 Dimensional Moulding Process

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Keywords: Compression, densification, end grain, forming, moulding, recovery

ABSTRACT

The densification of wood leads to a new material with high strain. The material behaviour can be described as viscoelastic material like foam. After the wood densification we receive more than 50% strain in order of the compression ratio. The modification procedure can be described in three steps: heating, densification and cooling. To influence the mechanical properties it is possible to choose the process parameter. The processes take place in a conventional multistory hot press with. In order to test limited range it was choose different temperature, moisture, pressure, speed and wood species [Haller 2004]. Several tests were carried out with wood cubes in labor conditions. One of the requirements to get a formable material needs a homogenous densification profile. The cell walls will be folded continuous through the whole cross section. The folded cell walls are not stabile and it is possible to recover. The process of forming material will use this strain potential. Against the aim of different working projects to produce a material with high dimensional stability of densified wood, will be used the deformation as a charged energy inside the wood structure. The densification is required as a first step to produce a high potential of strain. After the wood processing from the single cube to the end grain board will be molding the second step of shaping. The new formed board is to dry and to fix in the last step. The process to use the spring back of wood is possible with high temperature and moisture. The compressed material could be recovered with a treatment in boiling water or under a saturated steam atmosphere. Depends of the degree of densification is the recovering potential theoretical more than 50% in terms on the densified material. The objective of several test were to find out the optimal relationship between the process parameter (degree of densification, moisture, temperature, compression speed), the material properties (density, wood species, annual rings) and the homogenous strain potential.

INTRODUCTION

The development of a new technology to mould boards in multiaxial shapes founded on the understanding of the thermoplastic behavior of wood (Dinwoodie 2000). Probably the most well known technology is the one introduced by Thonet during the last century, bending wood parallel to the grain for the manufacturing of furniture. To be softened, the bending good was steamed and heated.

MATERIAL AND METHODS

The aim was to use the high strain from compressed wood for molding process perpendicular to the grain. All specimens were densified in one or two directions (Figure 1). During the process it was designed a new biaxial densification device. The densification behavior to analyze by testing of 11 parameters on more than 300

specimens was carried out. Each cube was stamped with 5 by 5 mm grid of the wooden surface. By using that method it will reduce small inhomogenous areas and the calculation effort. The grid deformation showed the main displacement of crossing points and the distance of it can be automatically calculated. The same way was used by the determination of recovery. The cubes were sliced by 10mm thick and fixed in water with 25°C. The recovery was measured up to 3600 seconds and the extension compared to the time. In general will recover each densified specimen about to 100%, however the speed can be a parameter of the forming quality.

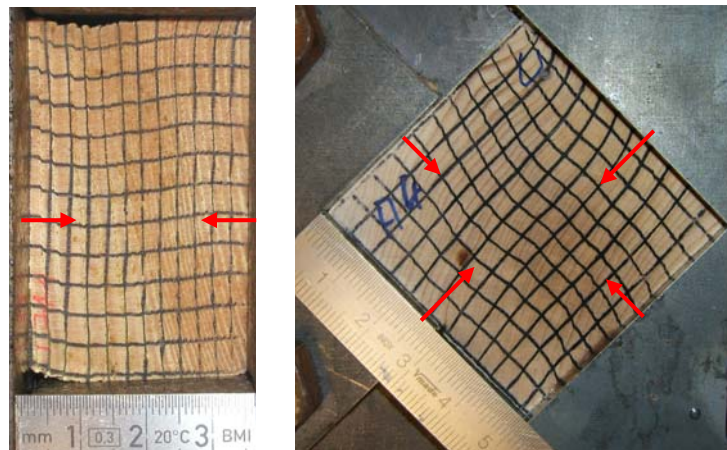


Figure 1: Surface of uniaxial densified (left) and biaxial densified specimen (right) with grid displacement and densification direction.

To investigate the molding potential, it was necessary to determine the optimum of the densification process. The tests were carried out mainly with three wood species from table 1. The moisture content of wood was 8 and 16% or conditioned in the normal climatic, depends of the testing parameters.

Table 2: Test parameter and short title in parenthesis.

wood specie	compress speed	temperature	moisture	densification
Poplar (Pa)	1mm/min (V1)	100°C (T1)	8% (H1)	30% (K1)
Spruce (Sp)	4mm/min (V2)	130 C (T2)	16% (H2)	50% (K2)
Lime (Li)				

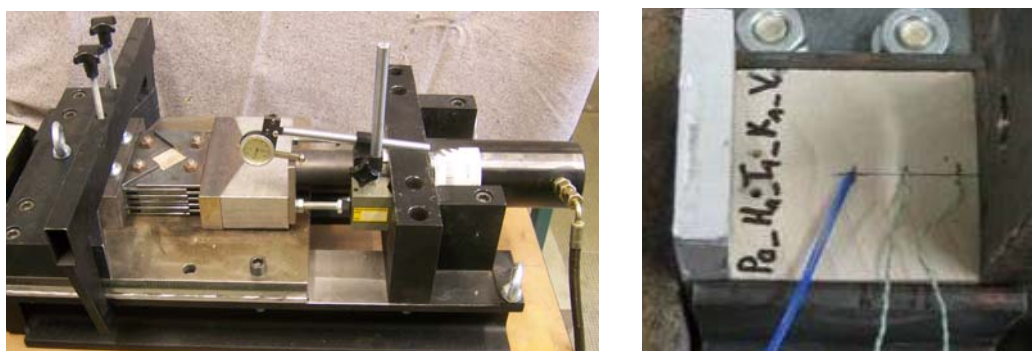


Figure 2: Hot press with biaxial densification device (left) and specimen with three temperature sensors (right).

The densification was carried out in a special hydraulic laboratory hot press and designed biaxial compression device (Figure 2). The parameters of the manufacturing

process, heating – compressing – cooling, are shown in figure 2 as example for lime. The densification direction was one- or biaxial and never parallel to the grain. The press plate temperature was 140°C. The other test parameters were described in Table 2. The geometry for densification tests was 60 x 60 x 50 mm. The temperature was measured on three points: 3.0, 12.5 and 25.0 mm from the edge. Additionally was designed a stamp grid of 5mm to better determine the densification profile. In the Figure 3 is shown the densification process of spruce with a speed of 4mm/min and the moisture content from 16%. The specimen surface is marked with 121 coordinates. The biaxial densification will be achieved due to the displacement of engaging metal plates. Influenced by the direction of annual rings was measured the distance in close proximity coordinates x, y and xy. This procedure was done by the densification and by the recovery.

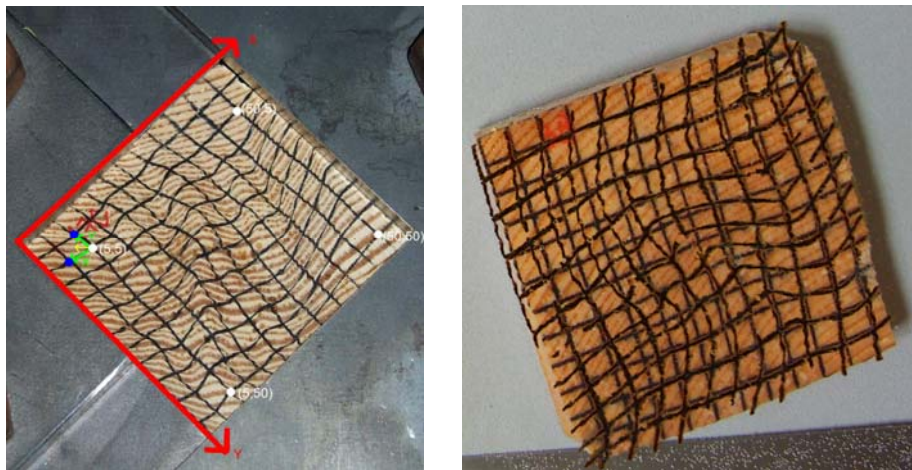


Figure 3: Definition of coordinate system(left) during the densification and displacement evaluation of the cross points (right) during the recovery (deformed grid was stretched to get the same size of specimen after 30 and 1800 seconds).

RESULTS AND DISCUSSION

The Figure 3 shows the concentration of deformation in the middle parts of cubes. Two important aspects affected the densification profile: a) moisture, b) annual rings. By further densification will achieve a homogenous displacement with high density. The cell walls will lay each other and glued together after the lignin plastification. It reduces the recovering behaviour. The influence of steam pressure was measured after 1800s by increasing centre temperature. Specimen with more than 90°C had a soft compression behaviour as well as specimen with more than 100°C. In any case the wood cells were irrelevant deformed to the first 3mm. In particular the wood specimens T2 (50%, 130°C) evolves two density maximum by 2/5 and 4/5 about the thickness. Besides has higher moisture content more recovering potential (90%) and needs lower compression ratio. The spring back will increase with dry specimen and reduced the remained deformation. The compression speed was not significant of the strain reserve. The tendency showed that low temperature, high moisture and pressure will achieved maximum degree of densification. The best recovering to produce leads however to find optimum in more parameter like grain direction, volume of pores, temperature etc. The results of recover behaviour were very different. In general had the high moisture content with the low temperature level the maximum recover potential. The reason might be less cell wall gluing with high flexibility because of higher moisture. The reactivation of utilize deformation represented in Figure 4. The influence of different

parameters will affect the uniaxial as well as the biaxial recovery. The special investigation described the process parameter, which affected the recover potential in one or two directions. To use the innovative process was it necessary to find the optimum performance between the material parameter and the production possibilities. There are two ways to use the recover behaviour of wood: unidirectional densification to mould hollow wood profiles or to take the bidirectional densification to mould multidimensional end grain board. Moulded wood profiles and boards are efficiently products to replace wood in same kinds.

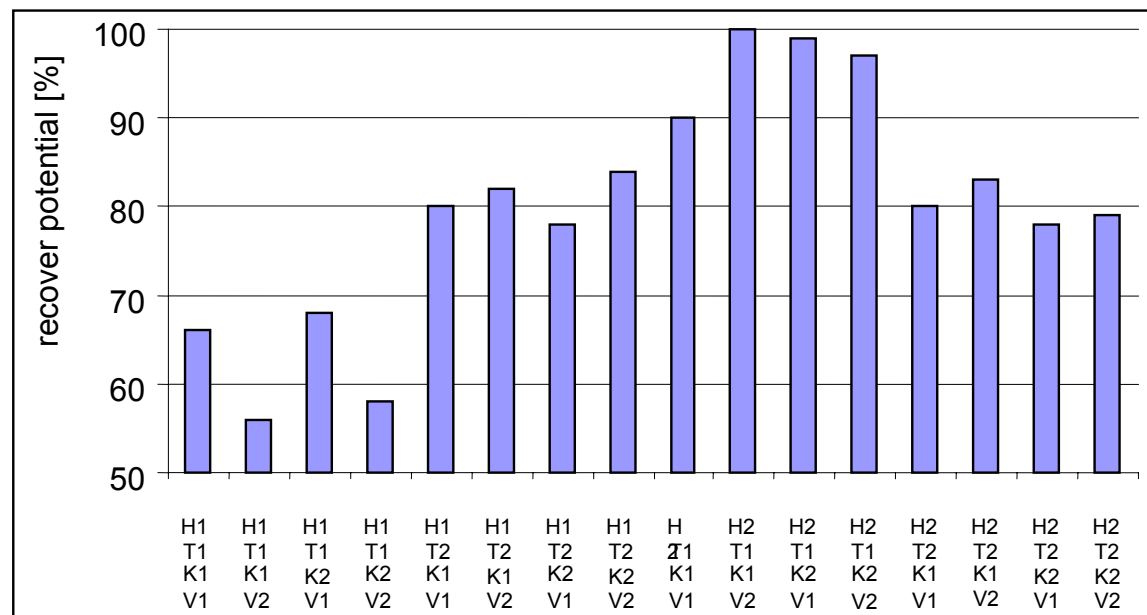


Figure 4: Comparison of different recover potential [%] of black poplar (H=moisture, T=temperature, K= densification, V= speed)



Figure 5: Moulded end grain board (a) and uniaxial densified half pipe (b)

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The Changes in Physical and Mechanical Properties of Alder and Spruce Wood as a Result of Thermal and Thermo-oil Modification

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Keywords: hygroscopicity, natural oil, resistance to fungi, strength, thermowood,

ABSTRACT

Thermally and thermo-oil modified wood is usually less hygroscopic, more dimensionally stable, more durable and resistant to fungal decay caused by *Basidiomycetes* fungi than natural wood of the same, susceptible to decay species. The resistance of such modified wood to filamentous fungi belonging to *Ascomycetes*, *Deuteromycetes* group, which may cause mould and soft rot of wood, is not so evident. Besides, changes in wood properties resulting from thermal modification strongly depend on thermal and moisture conditions of thermal modification process. We tried to obtain improved wood in semi-laboratory conditions by means of thermal modification carried out also as a heat-oil treatment. The changes of chosen physical and mechanical wood properties and resistance of wood against mould fungi, resulting from thermal or thermo-oil modification treatment of wood, were the subject of the study, determined and described. Samples of alder - *Alnus glutinosa* and Norway spruce – *Picea abies* were the object of the study.

INTRODUCTION

Impregnation of wood with natural oils connected with thermal treatment of wood are a method made for improving some functional properties of wood. Thermally and thermo-oil modified wood is usually less hygroscopic, more dimensionally stable, more durable and resistant to fungal decay caused by *Basidiomycetes* fungi than natural wood. The resistance of such modified wood to filamentous fungi belonging to *Ascomycetes*, *Deuteromycetes* group, which may cause mould and soft rot of wood, is not so evident. [Fojutowski *et al.* 2009]. The dimensional stability of the wood is often improved. These kind of wood modification is an alternative to application of biocides and it enables to use wood in higher service classes requiring increased durability [Fojutowski *et al.* 2009, PN-EN 335-2, PN-EN 350-2]. Thermal (~200°C) modification may cause a decrease in wood durability by influencing on the possibilities of use of this wood in load bearing structures [Bengtsson *et al.* 2002]. We tried to obtain improved wood in semi-laboratory conditions by means of thermal modification carried out also as a thermo-oil treatment. The aim was to identify the effect of thermal modification and thermo-oil modification and impregnation with natural oil of alder – *Alnus glutinosa* and Norway spruce – *Picea abies* wood on their physical and mechanical properties and resistance to fungi causing mould on wood. Thermal modification and oil impregnation of the wood may broaden possibilities of practical use of the wood which are not durable enough.

MATERIALS AND TEST METHODS

The materials used in the tests consisted of alder wood (*Alnus glutinosa* (L.) Gaertn.) and Norway spruce (*Picea abies* (L.) Karst.) little beams which were planed on four surfaces and had sharp edges – 40R(thickness)x145Tx650Lmm. Besides of control wood (C-not treated) the beams were subjected to:

- O - vacuum-pressure impregnation with technical linseed oil of the temperature of 65°C and density of 0.928 g/cm³ which contained 75% of linoleic (C₁₈H₃₂O₂) and linolenic (C₁₈H₃₀O₂) acids,
- T - thermal modification at the nominal temperature of 195°C and
- TO - thermal modification and following impregnation with technical linseed oil, as mentioned above. Samples cut out of the little beams were conditioned for testing in normal conditions (20°C/65%) till equilibrium moisture content was reached.

Determinations of the following physical - mechanical characteristics were carried out: equilibrium moisture content of samples conditioned till a constant mass in normal conditions (20°C/65%) is reached, by oven dry method [PN-EN 13183-1] and absorbability after 48 h of soaking in water; density – by stereometric method [PN-77/D-04 101]; bending strength and modulus of elasticity at three-point bending [PN-77/D-04 103, PN-77/D-04 117]; parallel to grain compression strength [PN-77/D-04 102]; impact bending strength [PN-77/D-04 104].

A method adapted from building procedures [Instrukcja ITB...1995] was used for mycological testing. Test and control samples were exposed to the following fungi: Set I = Mixture of: *Aspergillus niger*, *Penicillium funiculosum*, *Paecilomyces varioti*, *Trichoderma viride*, and *Alternaria tenuis* or Set II: *Chaetomium globosum* fungus; incubation at the temperature of 27±1°C and relative humidity of 90%. After 4 weeks the growth of mycelium on the surface of test samples was evaluated using the following scale:

0 – lack of visible under the microscope fungus growth on a sample, 1 – minute growth, barely visible to the naked eye (=WNO) but well visible under the microscope or WNO growth limited to the edges of a sample only, 2 – WNO fungi growth on a sample but less than 15% of the surface is covered with fungus, 3 – over 15% of the surface is covered with WNO fungus. A standard evaluation was completed with estimation of percentage of a sample surface overgrown by mycelium. The test samples of the dimensions of 60x20x3(thickness)mm were individually placed on Petri dishes of the diameter of 100mm and outside height of 15mm. For each variant of tested wood 6 samples were used.

TEST RESULTS AND THEIR DISCUSSION

Equilibrium moisture content of wood (Table 1) decreased very distinctly from around 11-12% for natural wood to the level of about 7% for impregnated with oil (O) or thermally modified alder wood (T) and 4% for thermo-oil modified (TO) alder wood and respectively to the level of about 11% (O), 7% (T), 6% (TO) for spruce wood. It indicated strong hydrophobization of wood by oil and thermomodification (Table 1). Thermal modification decreased density of wood (Table 2) to 98% - alder or 92% - spruce of initial value. Impregnation of both species of wood with oil and their thermo-oil modification increased their density in relation to the value of natural wood but the increase in alder wood density was much greater than in spruce wood, probably as a result of much greater retention of oil in alder wood. Bending strength of T and TO wood decreased, for alder wood even to the level of 70 % and 86% of the value

characterising natural wood, however MoE at bending for both wood species modified as O,T and TO were greater than this of natural wood. Parallel to grain compression strength of tested wood increased from 106 to 120% besides of spruce wood O for which the drop of strength to 94% of natural wood was stated. Impact bending strength of alder and spruce O, T and TO wood decreased, even to the level of around 34% of this strength value characteristic of natural wood for alder TO wood.

Table : Equilibrium moisture content [%] of wood at normal condition: 20°C, 65% RH

Tested wood	Before modification - C ^a		After modification	
	O ^b	T ^c	TO ^d	
Alder	10.8	7.0	6.7	4.5
Spruce	12.4	11.0	7.2	5.8

^a Control, ^b O impregnation with oil- retention of oil: alder 329 kg/m³; spruce 35 kg/m³, ^c T – Thermal modification, ^d TO – Thermal-oil modification – retention of oil: alder 272 kg/m³; spruce 59 kg/m³

Table 2 Physical and mechanical properties of modified alder and spruce wood

Wood	Density [kg/m ³]	Absorbability [%]	Bending strength [N/mm ²]	MoE ^e [N/mm ²]	Compression along grain strength [N/mm ²]	Impact [J]
Alder C ^a	543	66.8	83.0	7861	49.3	5.3
Alder O ^b	867	18.7	89.4	8376	52.1	4.1
Alder T ^c	534	52.4	71.4	9598	59.4	2.1
Alder TO ^d	750	24,9	57.8	8216	53.2	1.8
Spruce C ^a	413	56.1	58.0	6202	39.2	4.0
Spruce O ^b	422	55.9	57.8	6636	37.0	2.1
Spruce T ^c	380	66.8	54.9	8246	45.7	2.0
Spruce TO ^d	433	51.9	54.9	7131	45,8	2.2

Legend for ^a to ^d as for Table 1, ^e Modulus of elasticity by bending

Results of visual assessment of wood resistance to mould fungi presented in Table 3 and 4 shows that the growth of fungi mixture and the growth of *Chaetomium globosum* mostly reached the highest 3. degree on tested and control specimens. The grade 2.2 was the smaller one, but it indicated also that tested wood has to great ability for fungal growth. According to criteria used in buildings such materials are rated among not resistant to mould fungi. Mean growth of the Mixture of fungi on thermal and thermo-oil modified alder and spruce wood was 90% to 100%. The growth of the fungi on spruce and alder wood impregnated with oil was not so great, it ranged from 20% to 60% compared with 90 -100% on control wood. Control spruce wood unexpectedly was covered in the test with Mixture of fungi by only 20%.

Heat treatment and heat-oil treatment had no significant effect on the grade of fungi Mixture growth on wood. Mean growth of *Chaetomium globosum* fungus on thermal and thermo-oil modified Scots pine was also almost the same as on control wood. The effect of impregnation of wood with oil in terms of resistance against mould seems to be better than thermo- and thermo-oil modification of wood. The resistance of wood against mould fungi on thermo-oil modified wood are however not good. So there is no clear connection between retention of oil and grade of fungi growth on oil or heat-oil treated wood. Thermal and thermal-oil modification of alder and spruce wood did not distinctly decreased the intensity of fungi growth, both the Mixture and *Chaetomium globosum*, on wood surface.

Table 3: The resistance of thermal modified and thermo-oil (linseed oil) modified alder and spruce wood to mould fungi – test acc. to Building Research Institute Instruction [Instrukcja ITB 355/98] using the Mixture of mould fungi – Set I

Wood	Mean grade of fungal growth	Mean ^e fungal growth on sample surface [%]
Alder C ^a	3.0	90
Alder O ^b	3.0	60
Alder T ^c	3.0	100
Alder TO ^d	3.0	100
Spruce C ^a	2.7	20
Spruce O ^b	3.0	60
Spruce T ^c	3.0	100
Spruce TO ^d	2.8	90

Legend for ^a to ^d as for Table 1, ^e number rounding to 10%

Table 4: The resistance of thermal modified and thermo-oil (linseed oil) modified alder and spruce wood to mould fungi – test acc. to Building Research Institute Instruction [Instrukcja ITB 355/98] using the *Chaetomium globosum* fungus – Set II

Wood	Mean grade of fungal growth	Mean ^e fungal growth on sample surface [%]
Alder C ^a	3.0	90
Alder O ^b	3.0	60
Alder T ^c	3.0	100
Alder TO ^d	3.0	100
Spruce C ^a	3.0	90
Spruce O ^b	2.2	20
Spruce T ^c	3.0	90
Spruce TO ^d	2.8	100

Legend for ^a to ^d as for Table 1, ^e number rounding to 10%

CONCLUSIONS

In comparison to natural wood thermally modified and thermo-oil modified alder and spruce wood demonstrates an increase in compression strength and modulus of elasticity at bending where at the same time bending strength and impact bending strength are decreased. An increase in hydrophobicity of wood may be expected as a result of thermal modification and thermo-oil modification of alder and spruce wood. Thermally modified and thermo-oil modified alder and spruce wood demonstrates a similar to natural wood lack of resistance to growth of mould fungi on its surface. However in comparison to natural wood the grade of growth of mould on the surface of wood treated only with oil was less.

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Surface Properties of the Hydrothermally Modified Soft Deciduous Wood

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ABSTRACT

Surface free energy of wood is an important parameter in fields like coating, painting and gluing, although it is complicated since it is not a directly measurable quantity. The simplest technique that can help us is contact angle. In this work, the effect of thermal treatment on surface free energy of two wood species has been investigated. Aspen and grey alder samples have been treated at different temperatures and times, then contact angle data have been collected and used to determine the surface energies. Three probe liquids have been used. There are many controversies about the correctness of one theory respect to others, due to differences in the mathematical approaches, but mainly due to the choice of the components of the surface energy. We compare the most commonly used approaches: Zisman, Owens-Wendt, Wu, Equation of State and Acid-Base theories. The results demonstrate that heat treatment concretely affects the surface wettability. Detailed information came from the Owens-Wendt, Wu and Acid-base theories: the polar component decreases with higher temperatures, the dispersive component is more stable and predominant. Measurements have been conducted trying to fulfil the same conditions; in any case, it was not possible to reach the conditions assumed by Young's equation, due to wood surface nature.

INTRODUCTION

Thermal treatment is a widely investigated sector. Such a treatment affects all the chemical-physical properties of wood, compared with fresh and untreated (Kocaefe *et al.* 2008, Andersons *et al.* 2008) In particular we focused on changes in wood wettability, which has a practical relevance and economic significance. Wettability is strictly connected with coating, painting and gluing, procedures that can be enhanced from the comprehension of wetting behaviour after thermal modification. To understand the wetting of wood we need to study the surface free energy of wood, as already indicated in other publications (Kocaefe *et al.* 2008, Scheikl *et al.* 1998, Good 1992) and the most widely used technique for this aim, is contact angle measurement. Surface energy corresponds to the change of the total surface free energy (G) per surface area (A) at constant temperature (T), pressure (P) and moles (n) (Eqn. 1):

$$\gamma_s = (\delta G / \delta A)_{T,P,n} \quad (1)$$

However, it's not directly measurable: its estimation comes from solving the Young's equation (Eqn. 2):

$$\gamma_{lv}\cos\theta_Y = \gamma_{sv} - \gamma_{sl} \quad (2)$$

and additional relations to determine γ_{sv} and γ_{sl} . These relations are at the base of many theories concerning contact angle, among them we used the Wu (Wu 1971), Owens-Wendt (Owens, Wendt 1969) and Acid-Base approaches (van Oss et al. 1988), which belong to the components theories, and the Zisman (Zisman 1963) and Equation of state (Neumann *et al.* 1974) approaches, which are one component theories. There are many controversies about the correctness of these approaches also because in some cases can be used only in particular conditions of surface and liquids. For wood surfaces, contact angle measurements are made more complicated for the complex nature of wood itself: Young's equation represents an ideal situation, surface is smooth and contact angle has a single value, but for wood surfaces these conditions cannot be achieved. Roughness and chemical heterogeneity affect measurements, giving place to contact angle hysteresis phenomena (Li 1996, Chibowski *et al.* 1993). Wood is also a porous and hygroscopic, this leads to swelling, reactions and contamination of liquids by wood extractives (Wålinder *et al.* 2000). To obtain meaningful values of contact angle, surface must be as smooth as possible: we opted for surface sanding before any measurement. The aim of this work is to investigate how wettability changes after hydrothermal modification, and to evaluate the surface free energy using the previously cited theories.

EXPERIMENTAL

Material

Hydrothermally modified wood samples of grey alder and aspen at 160°C (treatment time: 1h and 3h), 140°C, 170°C and 180°C (treatment time: 1 hour) as also untreated samples, were stored in a climate chamber at 23°C and 63% rh, until they reached equilibrium moisture content. To obtain a smooth surface, sand paper with a fine grain size has been used: we sanded each sample, cleaned with a vacuum water pump to eliminate residual dust, and measured, immediately after sanding, contact angle perpendicular to the wood fiber direction. The liquids used in this experiment are water, glycerol and formamide. For contact angle measurements we used a Dataphysics OCA20 device, equipped with a video camera and software for the analysis of the drop shape, contact angle and solid surface free energy computation. The technique used for the measurements is the static sessile drop technique, which consists in deposition of a single droplet on the solid surface without any further addition of liquid, the device is equipped with an automated dispenser to have always the same volume of liquid (10 μ l water, 7 μ l glycerol and formamide). At least six droplets per sample have been measured; the final data are the average of all collected contact angles. We assume that the droplet reaches thermodynamic equilibrium when the difference with the previous contact angle is about of 1 degree: this angle was used for the solid surface free energy computation. As we already cited, wood is a porous material, each probe liquid penetrates with time into the wood and sorption causes swelling and lost of liquid from the droplet, both influencing the correctness of the measurements. For this reason angle must be measured as soon as possible, in order to avoid these negative parameters.

RESULTS AND DISCUSSION

In Table 1 the average contact angles are reported, the water gives the highest values, except for grey alder control, grey alder and aspen 140°C heat treated samples where glycerol has higher values. Formamide has always the smallest contact angle. From these data we computed surface free energy with five methods, see Table 2, and we can immediately see that the obtained results, for each method, are in a quite narrow range, except for the Acid-Base method, and they confirm that wood is a low energy solid.

Table 1: Average contact angle of aspen (AP) and grey alder (GA)

Sample	Water [°]	Glycerol [°]	Formamide [°]
AP180	99,04	79,46	63,46
AP170	85,11	79,08	64,13
AP160 3h	87,39	82,44	64,35
AP160	81,15	76,13	55,35
AP140	69,32	75,50	52,15
APcontr	62,06	59,63	36,65
GA180	99,02	79,63	72,19
GA170	89,42	72,14	66,28
GA160 3h	87,01	70,66	61,43
GA160	91,02	76,37	62,59
GA140	64,38	73,45	44,05
GAcontr	53,58	64,08	39,21

Table 2: Solid Surface free Energy (mJ/m²) of Aspen and Grey Alder wood samples

Wood Samples	METHODS											
	Zisman	Owens-Wendt			Wu			EOS	Acid-Base*			
	γ_c	$\gamma = \gamma^d + \gamma^p$	γ^d	γ^p	$\gamma = \gamma^d + \gamma^p$	γ^d	γ^p	γ	γ	γ^{LW}	γ^+	γ^-
APcontr	45,69	42,76	27,10	15,65	44,37	24,29	20,08	45,53	70,56	70,56	0,00	14,80
AP140	26,24	32,75	15,78	16,97	36,13	17,12	19,01	38,80	86,27	86,27	0,00	15,98
AP160	39,57	33,30	28,03	5,27	34,11	23,23	10,88	35,47	71,76	71,76	0,00	5,21
AP160 3h	33,11	28,07	24,00	4,07	29,75	20,62	9,13	31,32	59,92	59,92	0,00	4,04
AP170	31,55	28,41	23,08	5,33	30,43	19,70	10,73	32,36	46,56	46,56	0,00	5,18
AP180	44,15	46,51	46,48	0,03	40,11	38,82	1,29	30,16	43,80	43,80	0,00	0,00
GAcontr	25,25	44,11	14,06	30,05	45,67	18,07	27,60	46,39	85,30	85,30	0,00	27,89
GA140	33,81	36,26	17,19	19,07	39,13	18,82	20,32	41,80	115,25	115,25	0,00	18,01
GA160	40,75	36,77	35,62	1,14	33,70	27,54	6,16	32,08	41,86	41,86	0,00	1,19
GA160 3h	40,37	36,82	34,50	2,32	34,33	25,78	8,56	34,11	33,31	30,33	0,97	2,27
GA170	36,77	33,99	31,76	2,23	32,17	23,84	8,32	32,47	24,23	18,97	3,19	2,16
GA180	36,90	35,14	34,90	0,22	31,44	27,96	3,48	28,19	23,13	21,87	1,58	0,25

$$* \gamma = \gamma^{LW} + 2\sqrt{\gamma^+ \gamma^-}$$

If we analyze the obtained polar and dispersive components, we have two groups of samples: the first group, control and 140°C h.t. samples, which have more hydrophilic character and the second one, from the other samples, which have more hydrophobic nature. Even the contact angle values can confirm this choice, in fact for the first group samples, contact angle shows the lowest value and moreover water has sometimes lower contact angle than glycerol, thus confirming the high affinity for water and polar solvents.

CONCLUSIONS

Heat treatment clearly have influence on the solid surface free energy of wood, we can say that in general energy decreases from untreated to 180°C h.t. wood. For what concerns wettability, is clear how the wood becomes more hydrophobic for higher temperatures, and the polar component dramatically decreases, according to our data, thus the surface is more suitable for non-polar solvents. Results in some cases can be a little confusing, in particular from the Acid-Base approach, this could be due to the small number of used solvents. In any case, the chemical-physical properties of wood make impossible to fulfil the conditions assumed in the Young's equation, surface roughness, absorption and capillarity affected the measurements.

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Prediction of Mechanical Properties of Thermally Modified Beech Wood by Use of Near Infrared (NIR) Spectroscopy

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Keywords: Beech wood, FT–NIR spectroscopy, mechanical properties, thermal modification, air-dry density

ABSTRACT

NIR spectroscopy was used for the prediction of mechanical properties (modulus of rupture (MOR), modulus of elasticity (MOE)) and air-dry density of thermally modified beech wood (*Fagus moesiaca* C.). Thermal treatment of the samples was done under industrial conditions. NIR spectra were recorded from the cross-sections and radial surfaces of untreated beech wood from sapwood and red heartwood prior thermal treatment. The samples were divided into the part for cross validation and the part for testing of the model. PLSRs (Partial Least Squares Regression) were developed for air-dry density, MOR and MOE. The obtained coefficients of determination and errors of prediction are in the range from very good to moderate depending on the part of wood and the investigated wood property.

INTRODUCTION

Besides being an ecological treatment for the preservation of wood, thermal modification also improves its biological durability, the physical properties, the dimensional stability of wood, reduces its hygroscopy and consequently makes wood irreplaceable in variable conditions of exploitation (Militz 2002). Beechwood is the most important industrial hardwood species in the Balkan Peninsula and in spite of its good mechanical properties it is prone to deformities under variable conditions and climatic conditions of the environment. From the aspect of wood processing and use of beech wood the presence of red heartwood is particularly interesting as it is a less valuable part of the wood. With the optimal regime which can lead to no essential difference in the properties of thermally modified beechwood with red heartwood and sapwood the less valuable wood can, in that case, be used for getting highly valuable products. In order to achieve that, it is very interesting to determine the mechanical properties (MOR and MOE) of thermally modified beech wood with red heartwood. In that aim, NIR spectroscopy is a reliable technique for non-destructive determination of the properties of wood (Tsuchikawa 2007, Todorovic *et al.* 2009). NIR was also used as a tool for the determination of properties of thermally modified wood (Schwanninger *et al.* 2004, Esteves and Pereira 2008). Since NIR spectra consist of mainly overlapping bands of C-H- and O-H- overtones and combination bands, multivariate statistics has to be applied for evaluation. This study uses partial least squares regression (PLSR) to evaluate MOE, MOR and air-dry density of sapwood and red heartwood of thermally modified beech samples (190°C 3 h) in an industrial scale kiln. This regime was chosen

as most frequently used regime for thermal modification of hardwood species (beech, oak sessile, ash) in the industrial conditions (Tarkett d.o.o. Serbia).

EXPERIMENTAL

Sample preparation

Thirty-three beech wood (*Fagus moesiaca* C.) logs were harvested at the locality Goč in Western Serbia. Boards approximately 3 cm wide and 1.8 m long were cut from the log cantered on the pith. After kiln drying (max temp. 50°C), the boards were planed to a final thickness of about 2 cm. The final dimensions of the bending samples were 320 x 20 x 20 mm³ (axial x radial x tangential). Samples were divided into two groups: sapwood and red heartwood. Thermal treatment of the samples was performed under industrial conditions with hot air at the temperature of 190°C for 3 hours. After the heat treatment the samples were kept in a conditioned room at 23±3°C and 50±3% relative humidity for three weeks prior to analysis.

FT-NIR spectroscopy

FT-NIR measurements were made on the cross-section and radial-longitudinal wood surface. Spectra were collected prior thermal treatment with a Nicolet Nexus 670 FT-IR spectrometer equipped with a Thermo Nicolet Smart Near-IR UpDrift probe in the wavelengths range from 1000–2500 nm using the default parameters. The diameter of the measurement spot is 7 mm. For each scanning point, 100 scans (8 cm⁻¹) were collected and averaged into a single spectrum, 8 spectra were collected from each sample from the radial-longitudinal surface, and 4 spectra were collected from each sample from the cross sectional surface. Prior to multivariate analysis, the four spectra were averaged producing one spectrum per specimen from cross-section and eight spectra were averaged producing one spectrum per specimen from radial-longitudinal surface. The single cross-section and radial-longitudinal spectrum were used for calibration and to predict the mechanical strength and air-dry density of the individual samples.

Mechanical properties

After thermal treatment, modulus of elasticity (MOE) and modulus of rupture (MOR) of 92 samples of sapwood and 91 samples of red heartwood were measured according to SRPS D.A1.035 (MOE) and SRPS D.A1.046 (MOR). Density was determined according to SRPS D.A1.044. All of the samples were broken with load applied against their radial surface. The statistical descriptions of air-dry density, MOE and MOR are shown in Table 1.

Table 1: Statistical description of thermally modified (190° C 3h) beechwood air-dry density (g/cm³), MOE (N/mm²) and MOR (N/mm²)

Wood properties	Sapwood				Red heartwood			
	Mean	Maximum	Minimum	SD	Mean	Maximum	Minimum	SD
Air-density	0.681	0.789	0.601	0.043	0.692	0.806	0.551	0.059
MOE	11359	18470	7177	2391	10765	18250	7200	2465
MOR	94	132	66	14	89	139	49	18

PLS Regression

Two-thirds of the samples were selected as the calibration set and one-third was selected as the prediction set (test set) from both of parts of the wood. The models were

constructed for: air-dry density, MOR and MOE. The spectra were converted to the first-derivative mode (Norris - Gap and Savitzky - Golay with 13 points) to eliminate the influence of instrument background and drifting on signals. The best models were chosen and shown. Full spectral range (1000-2500 nm) was used. For spectral pre-treatment and PLS-1 regression the Unscrambler 9.7 (Camo Process AS Oslo, Norway) was used. Calibrations were developed using PLS-1 analysis. The standard error of calibration SEC (determined from the residuals of the final calibration), and the coefficient of determination (r^2_{cal}) were used to assess calibration performance. The standard error of prediction (SEP) and the coefficient of determination (r^2_{val}) gave a measure of how well a calibration predicts the properties of unknown samples. RPD (ratio of the standard deviation of the reference results to SEP) is a measure of the predictive ability of a NIR calibration. If the SEP is close to the SD, then the NIRS calibration is not efficiently predicting the composition or functionality (YU *et al.* 2009). RPD greater than 2.5 is considered satisfactory for screening, although it has been shown that with the RPD of approximately 1.5, NIR spectroscopy can be used as the initial screening tool (YU *et al.* 2009).

RESULTS AND DISCUSSION

The PLSR model parameters of thermally modified sapwood differ from the red heartwood of beech samples (Table 2). Generally the models of thermally modified sapwood samples showed better r^2_{val} and SEP values than red heartwood but they were not superior. The models of MOE, MOR and air-dry density based on the cross section spectra performed better than those based on the radial surface. All models of MOE show r^2_{val} values of > 0.72 for sapwood and > 0.50 for red heartwood for calibration and validation models. The r^2_{val} values of MOR are lower namely > 0.47 for sapwood and > 0.55 for red heartwood. Air-dry density could be modelled with an $r^2_{val} > 0.61$ for sapwood and for red heartwood > 0.50 (calibration and validation).

Table 2: Summary of PLS-1 model parameters of calibration and test set validation of MOE (N/mm²), MOR (N/mm²) and air-dry density (g/cm³) from the averaged spectra taken from the cross-section and the radial surface of the bending test.

Part of wood	Cross-section						Radial surface					
	N	r^2_{cal}	SEC	r^2_{val}	SEP	RPD	N	r^2_{cal}	SEC	r^2_{val}	SEP	RPD
NIR-MOE												
SW	5	0.90	472.1	0.79	822.9	2.3	5	0.90	571.9	0.72	669.9	2.9
RHW	6	0.94	1033	0.74	1615	1.2	6	0.88	1231	0.50	1780	1.1
NIR-MOR												
SW	4	0.91	4.44	0.71	6.13	1.8	4	0.89	5.03	0.47	7.15	1.5
RHW	6	0.89	4.63	0.60	8.14	1.5	5	0.90	5.78	0.55	9.12	1.3
NIR-Air-dry density												
SW	5	0.93	0.012	0.80	0.02	2.2	4	0.90	0.014	0.61	0.017	2.1
RHW	6	0.81	0.04	0.74	0.03	1.7	3	0.80	0.025	0.50	0.040	1.5

N-number of PLS factors, *SEP*-the standard error of prediction, *SEC*-the standard error of calibration, *SW*-sapwood, *RHW*-red heartwood, r^2_{cal} -coefficient of determination of calibration, r^2_{val} -coefficient of determination of validation,

The superior results of the transverse surface can be related to the fact that the scanned cross section contains large vessels of the ring wood. Besides, wide rays of the radial surface of the beech wood can influence the acquisition of the NIR spectra less than on the transverse surface. The SEP of the models based on the cross section and sapwood

spectra is lower than the SEP from the models based on radial surface and red heartwood spectra. The RPD is > 1.5 for all MOE, MOR and air-dry density except for MOR and MOE of red heartwood. Thermally modified red heartwood shows RPD values > 1.5 for air-dry density and MOR from cross-section but the values are lower than for sapwood. It is known that MOR is linked to MOE and wood density. NIR is sensitive to both parameters as well as chemical composition, however MOR is not described equally well (especially for red heartwood). One reason could be the influence of internal cracks in the cell wall structure induced by thermal treatment.

CONCLUSIONS

The results indicate that NIR spectroscopy and PLSR can be used for quality control of thermally modified beech wood which contains red heartwood. The obtained results are particularly significant if we take into account the fact that the recording of spectra was carried out on untreated samples, meaning prior thermal treatment. Such procedure of determining the properties of thermal wood can be very useful in on-line sorting of sawn timber before thermal treatment and it can contribute to better utilization of both sapwood and red heartwood as the less valuable part of such wood. Further research could be focused on the investigation of chemical properties of red heartwood after thermal treatment and assessment of its values by use of NIR.

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Chemical Modification of TMP for High Performance Fibreboards

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Keywords: Chemical Modification, DMDHEU, Fibreboard, Long term stability, Melamine

ABSTRACT

Medium Density Fibreboards (MDF) are not suitable for the application in high humid areas or in outside weathering conditions. High performance properties were achieved for MDF through a chemical treatment with the N-methylol-compounds 1,3-dimethylol-4,5-dihydroxyethylene urea (DMDHEU) and N-methylol-melamine (MF). The fibre treatment was performed in two steps: first, the water solved chemicals were sprayed on the fibre surface in a blender and subsequently the chemicals were cured in a fibre reactor above 100°C under vacuum. The amount of chemicals applied amounted to 10% and 20% solid content related to absolute dry wood mass. MDF of 9 mm thickness and a density of about 800 kg m⁻³ were manually produced with emulsified polymeric isocyanate (pMDI) adhesive at about 6% resin level. The boards fulfilled the requirements of EN 622-5 HLS [Boards subjected to high stress applications in wet indoor areas] regarding internal bond strength after 2h boiling in water. While the minimum standard requirement is 0.15 N mm⁻², the 20% MF-treated samples displayed 1.61 N mm⁻². Thickness swelling after 24 h immersion in cold water was clearly reduced, too. This effect was a long term effect, which was measured after 10 cycles of 4 days immersion in water and 3 days drying at 60°C. Fibreboards produced from MF-modified fibres performed better in all mechanical tests than those from DMDHEU-treated. This is attributed to stronger brittleness of DMDHEU-treated fibres, which might have lead to minor strength of single fibres and shorter fibre length after the modification process.

INTRODUCTION

Various processes for improving dimension stability of wood based panels had been investigated. Using of low hydrolyse effective adhesives such as phenol-formaldehyde resin (PFR) or application of pMDI enhance the bond line performance but are ineffective to improving wood matrix properties (Dunky and Niemz 2002). Some inorganic composites bonded with gypsum or cement were able to reach the step to the market (Pampel and Schwarz 1979, Moslemi 1999). However, these products contain less amounts of wood material. Nowadays wood based composites for humid and more or less outside conditions are bonded with high amounts of thermoset resins instead of being chemically modified, for example products like Trespa-Meteon[®], Werzalit[®] and Delignit[®]. Chemical modification of strands, particles and fibres has been investigated since decades mostly with acetic anhydride or similar compounds (Klinga and Tarkow 1966, Arora *et al.* 1981, Youngquist *et al.* 1986). Today, acetylation of wood fibres seems to be close to commercialisation (Jones *et al.* 2009). The brand TRICOYA[®]

shows the effort to bring fibreboards made from acetylated fibres on the market. This article describes the treatment of Thermo Mechanical Pulp (TMP) from Scots pine with water soluble N-methylol compounds.

EXPERIMENTAL

Fibre modification

Scots pine (*Pinus sylvestris* L.) fibres which were obtained by a TMP process were chemically modified in two steps with DMDHEU (Belmadur ES 97000, BASF, Germany) or with MF (Madurit WM 840/75WA, INEOS Melamines GmbH, Germany). In case of DMDHEU, 5% (m/m) of a Lewis acid catalyst was given to the solution. The concentrations used were 10% or 20% (m/m) related to absolutely dry (atro) fibre mass. In the 1st step loosened fibres were sprayed with water-based solutions of the chemicals in a rotating drum. In the 2nd step chemicals were cured in a 'fibre reactor' (Figure 1) at 125°C to a final moisture content (MC) of 2%. The whole curing process was performed under vacuum. Subsequently, the modified fibres were loosened using a hammer mill without sieves to avoid agglomeration during the following gluing process.

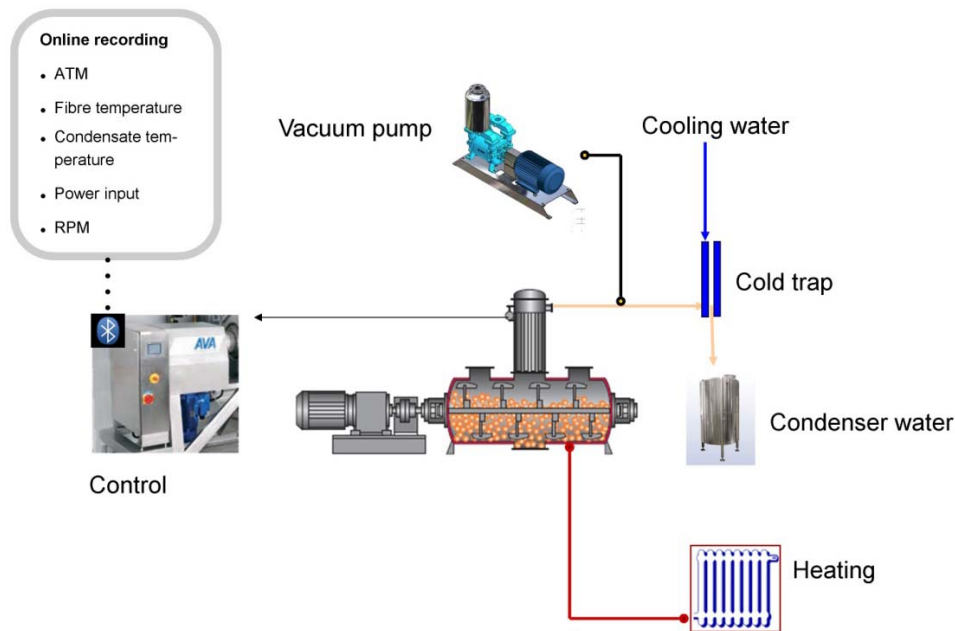


Figure 6: Fibre reactor for chemical modification at the University of Göttingen

Fibreboard production

Emulsifiable pMDI (I-BOND PB EM 4355, Huntsman, Belgium) at 6% (m/m) was sprayed on the chemically modified fibres in a rotary six angled drum. Prior to the gluing process the pMDI was emulsified with demineralised water to 50% solid content. Afterwards the glued fibres were aerated and hand moulded mats were formed. These were pressed to 10 mm (9 mm after sanding) MDF boards with 0.8 g cm^{-3} density at 15 s mm^{-1} pressing time. Adjusted temperature at an electrically heated single-daylight press (HP 200, Joos, Germany) was 200°C and pressure was set to 4.5 N mm^{-2} .

Mechanical properties

All samples were conditioned at $20\pm 2^{\circ}\text{C}$ and $65\pm 5\%$ RH for 2 weeks prior to the following tests. Modulus of elasticity (MOE) and bending strength (MOR) were determined according to the EN 310 (1993). Two sets of 4 specimens of $9 \times 50 \times 180 \text{ mm}^3$ ($t \times w \times l$) per treatment were cut from the fibreboards. Instead the boards were hand moulded; specimens were cut only in one direction of board dimension. Internal bond strength was determined after immersion in boiling water for 2h (IBB) according to EN 1087-1 (1995). Two sets of 8 specimens of $9 \times 50 \times 50 \text{ mm}^3$ ($t \times w \times l$) per treatment were cut from the fibreboards. After boiling the specimens were dried for 16h at $70\pm 2^{\circ}\text{C}$ in a drying cabinet according to EN 622-5 (2010). Finally, the specimens were glued on aluminium braces with a hot-melt adhesive in order to determine the internal bond strength.

Dimension stability

Thickness swelling (TS) was determined after immersion in 20°C water for 24h according to EN 317. Two sets of 6 specimens of $9 \times 50 \times 50 \text{ mm}^3$ ($t \times w \times l$) per treatment were cut from the fibreboards. After measuring the thickness, the specimens were stored in 20°C water for additional 48h. Two sets of 6 specimens were treated by the following steps in order to determine the long term stability of the applied chemical modification. The first step was immersion in 20°C water for 96h. The second step was drying for 72h at 60°C [1 week for 1 cycle]. This cycle was repeated for 9 times. Board thickness was measured prior to test, after water immersion and after drying, respectively.

RESULTS AND DISCUSSION

Treatment with both N-methylol compounds resulted in strong reduction of TS for both 24h and 72h immersion in water (Table 1). Accordingly there was a strong correlation between reduction of TS and concentration of the modification chemicals. Treatment with MF showed stronger reduction of TS as compared to DMDHEU. A decrease in MOR was observed with an increasing amount of chemical. However, reduction of strength was on a comparable level for both N-methylol compounds. Indeed, higher modification levels resulted in higher weight percent gains (WPG). A decrease in fibre length was observed due to modification and the loosening technique of the fibres. The high hydrophobic properties of MF (Landolt 1948, Trinh *et al.* 2009) were reflected by the stronger reduction of TS as compared to DMDHEU treatment.

Table 3: Thickness swelling MOR and MOE values of modified MDF

Specimens	Thickness-swelling 24h (%)	Thickness-swelling 72h (%)	MOR (N/mm²)	WPG (%)
Control	9.2 ± 0.8	13.0 ± 0.57	43.1 ± 7.3	-
Water treatment	9.0 ± 1.1	12.0 ± 0.8	43.5 ± 5.0	0.3
DMDHEU10%	7.5 ± 1.0	10.1 ± 0.8	37.3 ± 4.7	10
DMDHEU20%	6.0 ± 0.9	7.9 ± 0.9	35.7 ± 5.1	18
MF10%	5.0 ± 1.0	7.7 ± 0.5	37.5 ± 9.6	10
MF20%	4.0 ± 0.7	5.9 ± 0.5	34.7 ± 7.9	18

Figure 2 displays the increasing long-term dimension stability due to the chemical treatments. DMDHEU20% and both MF treatments showed the best performance in dimension stability. It is assumed that the molecules of both compounds are able to penetrate the cell wall; MF, however, seems to be more effective at same WPG. Accordingly TS of MF20% was constant after the third week at about 8% and that of DMDHEU20% at 10%. The higher performance in the IBB moisture resistance test (Figure 2) can provide an additional explanation for very low swelling rates. A strong fibre-fibre matrix is supposed to prevent water to penetrate the inner parts of the composites. One reason for the very strong increase in IBB could be a better wetting of the treated fibres with the pMDI adhesive; another reason could be the reaction of free formaldehyde with the adhesive. In case of MF a better compatibility with fibres and pMDI is assumed.

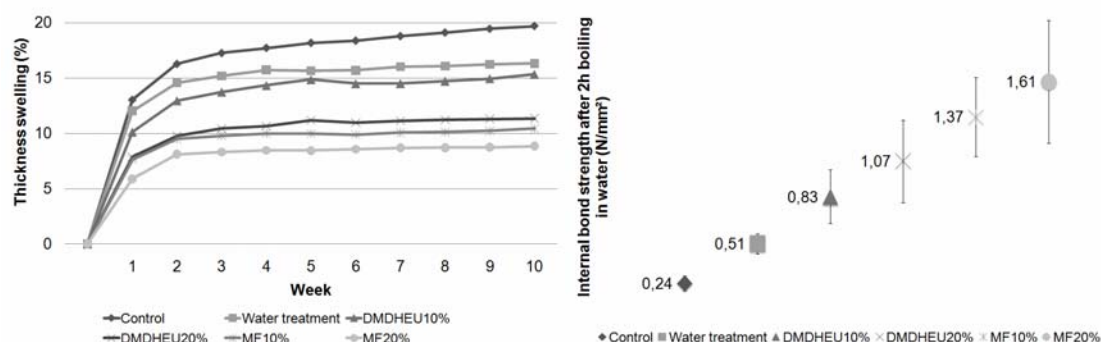


Figure 7: Thickness swelling after water immersion over 10 weeks (left) and internal bond strength after boiling in water (right)

CONCLUSIONS

Chemical modification of fibres with N-methylol compounds resulted in a strong decrease of short and long term thickness swelling. Decreasing MOR was probably a result of shortening of the fibre length, but an important increasing of internal bond strength under wet conditions was observed.

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Manufacture of Carbonized Board Using Medium Density Fiberboard and its Electromagnetic Wave Shielding Effects

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Keywords: Carbonized board, carbonization temperature, electrical resistivity, medium density fiberboard

ABSTRACT

The modified boards were made by carbonizing commercial medium density fiberboard (MDF) in a vacuum furnace. The carbonized boards did not show any cracks or deformation after carbonization. In this study, we investigated the effects of carbonization temperature on electromagnetic shielding characteristics and electrical resistivity of the carbonized fiberboards made by carbonizing the MDF of 0.45mm thickness between 400°C to 1,500°C. The carbonized fiberboards heated below 700°C showed lower electromagnetic shielding effectiveness between 10MHz and 1GHz frequency level. The carbonized fiberboards heated at 800°C and 900°C showed 43dB and 66dB on average, respectively. This means that the carbonized fiberboards heated above 800°C are useful as an electromagnetic shielding material. The carbonized fiberboard heated at 1,000°C showed remarkable electromagnetic shielding characteristics, namely the electromagnetic shielding effectiveness values of 1,000°C were 55dB at 10MHz, 60dB at 100MHz, 68dB at 200MHz, 78dB at 400MHz, 86dB at 600MHz, 93dB at 800MHz and 100dB at 1GHz, respectively. The carbonized fiberboard showed the highest electromagnetic shielding effectiveness at high frequency level. The carbonized fiberboard heated above 1,100°C also showed remarkable electromagnetic shielding effectiveness characteristics, namely the ESE values of the carbonized fiberboards were 80dB at 1,100°C, 83dB at 1,200°C, 83dB at 1,300°C, 84dB at 1,400°C and 84dB at 1,500°C on average. Significant changes were not found when the carbonized fiberboards are heated above 1,000°C. These remarkable electromagnetic shielding effectiveness of the carbonized fiberboards heated above 1,000°C were mainly due to the low electrical resistances (7.2~0.5Ωcm) of these carbonized boards. The carbonized fiberboards heated above 1,000°C could be used as a functional material for electromagnetic shielding.

INTRODUCTION

In today society there are a large number of electrical devices in use, these include televisions, cameras, computers, microwave ovens, cellular phones and so on. Electrical devices by nature produce electromagnetic waves when in operation. The transmission of these electromagnetic waves has many negative effects on the health of human beings and other living organisms. These harmful and undesirable effects may include tumors, leukaemia and other micronuclei damage. Therefore it is in the interest of the people's health to reducing the transmission of electromagnetic waves. In addition to the effects

on human health the emitted electromagnetic waves from one electric part or device may also be potentially damaging to another electrical devices. Therefore, it can be highly desirable to protect electrical devices from damaged by external electromagnetic waves. To prevent such damage, a shield can be used to diminish the transmission of electromagnetic waves. Considerable research on the electromagnetic dampening effects of charcoal has carried out for decades (Wang *et al.* 2003). It can be shown that the electromagnetic dampening effects of charcoal can be translated into carbonized wood and wood products. According to the research of Ishihara (1996 and 1999) and Wang *et al.* (2003), when wood is heated to a temperature reaching the stage of carbonization temperature (800°C~1700°C), the resulting charcoal can be used as an electromagnetic shielding material. Wood charcoal is typically laced with macro cracks. Those cracks have problems for industrial and commercial application. Kercher *et al.* (2002) made crack free carbonized medium density fiberboard(c-MDF) for electrical application. But there is no information relating to the electromagnetic shielding effects of the carbonized medium density fiberboards. This study was conducted to determine the electromagnetic shielding effects of the crack free carbonized medium density fiberboard.

EXPERIMENTAL

Carbonization of MDF

Medium density fiberboards (thickness 4.5mm, density 0.87g/cm³) were supplied by the SunChang company in Korea. They were cut into 40 x 40 cm² specimens. The boards were carbonized in a vacuum furnace. They were stacked in the furnace with graphite weight loading sheets between them to obtain an uniform specimen temperature and crack free boards. The basic thermal schedule was as follows: rate of temperature rise 100°C/h, carbonization temperature 400 ~ 1500°C, maximum temperature maintained for 2 hours.

Measuring of electromagnetic shielding effectiveness

The flanged circular coaxial transmission line method was used to detect the electromagnetic shielding effectiveness (ESE) of carbonized medium density fiberboard (MDF) according to ASTM D 4955-99. A Network Analyzer (HP 8720C) was used throughout this study to assess the electromagnetic shielding effects of the modified boards. The shielding effectiveness measurements are carried out for frequencies ranging from 10 MHz to 1000 MHz. The specimens were cut into “doughnut” shape inside diameter 76.2mm (±0.01mm), outside diameter 133.10mm(±0.01mm) and thickness 2mm.

Measurements of electric resistances

A digital multimeter DM-332, EZ Digital co., Ltd Korea was used to measure electric resistances from 0.1Ω ~ 400MΩ.

RESULTS AND DISCUSSION

Electromagnetic shielding effectiveness (ESE)

Carbonized wood is typically laced with macro-cracks due to the rate at which carbonization is performed by traditional carbonization method. But crack free c-MDFs were made by a new pressed carbonization method.

Figure 1 and table 1 show the electromagnetic shielding effectiveness of the carbonized MDF at various carbonization temperatures. The ESE increased with increasing thermoforming temperatures. ESE values of c-MDF carbonized at above 800°C temperature were higher than 40 dB in a frequency range of 10 MHz to 1 GHz. Generally 30 to 40 dB ESE values are acceptable in industrial and commercial application. ESE values of the boards heated below 700°C were less than 8 dB but constant across wide range of frequency. Average ESE values of c-MDF at 800°C and 900°C carbonization temperature are 43.06 dB and 66.76 dB respectively. This means that c-MDF processed at 800°C and 900°C carbonization temperature will be useful in commercial and industrial application. The MDF carbonized at above 1000°C carbonization temperature showed high ESE values of average 79.29 dB. Table 1 showed that ESE values of boards processed at above 1000°C carbonization temperature are not significantly different. Figure 1 showed that the ESE values at 1000°C are 55 dB in 10 MHz frequency, 60 dB in 100 MHz, 68 dB in 200 MHz, 78 dB in 400 MHz, 86 dB in 600 MHz, 93 dB in 800 MHz, and 100 dB in 1 GHz respectively. The ESE values at above 1000°C carbonization temperature showed similar increasing tendency according to an increase in frequency.

Table 1 : Average electromagnetic shielding effectiveness values of carbonized fibreboards.

Carbonization temperature(°C)	400	500	600	700	800	900	1000	1100	1200	1300	1400	1500
Ave. ESE(dB)	1.27	1.30	1.64	7.57	43.06	66.76	79.29	80.55	83.07	83.88	84.57	84.62

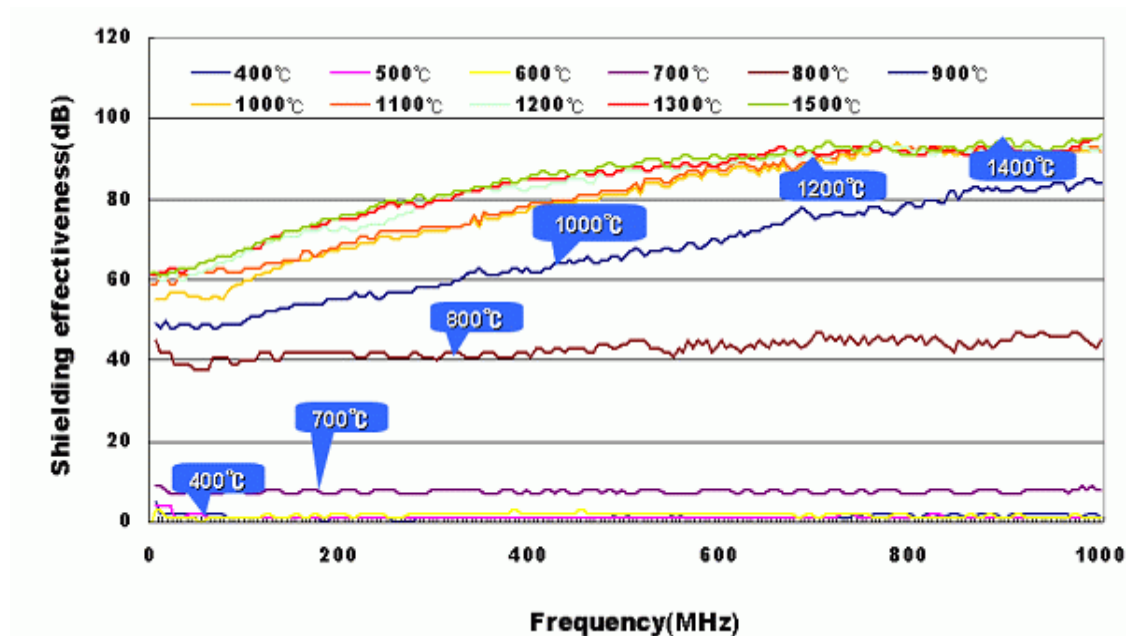


Figure 1 : Electromagnetic wave shielding effects of carbonized MDFs

Resistances of carbonized MDFs

Table 2 showed an electrical resistances for boards processed at various carbonization temperatures. We didn't measure the electrical resistances for boards processed below

400°C carbonization temperature. The resistance values decreased with increasing carbonization temperature, with significant reduction at above 800°C carbonization temperature. These results are in good agreement with previous report (Wang 2003). It is found that high ESE values at high carbonization temperature result from low electrical resistances. Therefore the MDFs carbonized above 1000°C temperature could be used as a multifunctional materials in commercial and industrial application.

Table 2 : Resistances c-MDF at various carbonization temperatures

Carbonization temperature(°C)	Resistance(Ω)	Carbonization temperature(°C)	Resistance(Ω)
400	Not measurable	1000	7.2
500	8.8×10^6	1100	6.5
600	180.9×10^3	1200	5.8
700	137.5	1300	0.5
800	13.4	1400	0.5
900	7.6	1500	0.5

CONCLUSIONS

The carbonized medium density fiberboards were made by heating commercially produced boards at various carbonization temperatures. The electromagnetic shielding effectiveness and electric resistances of the boards were measured. The carbonized MDFs heated below 700°C showed lower electromagnetic shielding effectiveness. However, c-MDFs processed above 1000°C carbonization temperature showed high electromagnetic shielding values, this was especially the case for the highest values at high frequency level. The resistances of c-MDFs above 900°C carbonization temperatures showed low values. Therefore, the c-MDFs heated above 800°C and 1000°C could be used as a multifunctional material for electromagnetic shielding.

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Dimensional Changes due to Water Sorption in High Wood-Content WPCs Prepared with Modified Wood

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Keywords: WPC, water sorption, dimensional changes, wood modification

ABSTRACT

Wood plastic composites (WPCs) are built up by a reinforcing wood component and a thermoplastic matrix which are efficiently combined and processed by thermoforming, e.g. extrusion, into a final shape. The dispersion of the wood component and resulting encapsulation by the thermoplastic will drastically reduce the rate of any moisture sorption in the composite, however, studies have shown that over time the moisture levels in the wood component could be sufficient for biological decay by fungi. The moisture sorption may also cause microstructural deformations with resulting dimensional changes and shape instability of the WPC product. By the use of a modified wood component these issues could be minimized or entirely avoided. The focus of this study was to investigate the water sorption ability and resulting dimensional changes of extruded WPCs with a comparable high wood content, i.e. ca 70 weight-%, prepared with either a heat treated, acetylated or unmodified wood component. Results show that the use of a modified wood component in these WPCs significantly reduces their water uptake and resulting dimensional changes. An effort was also made to determine the density of the wood cell-wall, in the actual composite and its relation to the applied wood modification route and moisture uptake.

INTRODUCTION

Wood plastic composites (WPCs) are in general composed of a reinforcing wood component combined with an olefin thermoplastic matrix. In this work we elaborate on using wood contents of up to 70 dry weight-% in the WPC. An important question that arise when applying such high wood-content levels in WPCs is, of course, how this influence their in-service behaviour in out-door use, in particular their water sorption properties and related dimensional stability? The general observation is that moisture uptake is slow in conventional WPCs compared with solid wood, even when immersed in water, but continues over a long period of time. Wang and Morrell (2004) have shown that moisture will not penetrate deep into the material, but the moisture levels close to the surface may be very high. A moist environment will swell the wood particles close to the surface, and the particles will shrink upon drying. This will cause stresses within the material and create microcracks, especially in the form of interfacial cracks between the wood and plastic components (Segerholm 2007), which may create new pathways for water intrusion deeper into the material. Regarding the use of very high wood contents, one critical problem is that an interconnecting network of touching particles/fibres may be created above a certain wood content threshold, following that the susceptibility to absorb moisture dramatically increases. To be able to use a high wood content in WPCs there is thus necessary to reduce the moisture sensitivity of the wood component, and one means for this is to use modified wood residuals in the WPCs instead of conventional unmodified wood residuals. One thing that we find important to

highlight in this work is that it is critical to know the wood component (or wood cell wall) density, in other words, the densities of the separate composite components plays a central role for the final density of the composite and also for finding suitable composite formulations with optimal volume fractions of the different components. Kellogg and Wangaard (1969) reported density values, determined pycnometrically in toluene, of dry softwood cell walls in the range of 1.48–1.50 g/cm³ (containing ca 2% voids), whereas Hill and Ormondroyd (2004) reported significantly lower corresponding values of 1.42 g/cm³ and 1.44 g/cm³ (based on helium pycnometry) for an unmodified and an acetylated softwood species, respectively. Some uncertainties of such measurements seem to exist, however, *e.g.* regarding effects of cell wall micropores, which are generally inaccessible to some displacement media in non-swollen cell walls. The objective of this paper is to present some observations about the water sorption ability and resulting dimensional changes of WPCs with a comparable high wood content, *i.e.* about 70 weight-%, prepared with either a heat treated, acetylated or unmodified wood component. An effort is also made in determining the wood cell wall densities in these composites.

EXPERIMENTAL

The wood raw material used in this study was prepared from acetylated and unmodified boards of Scots pine (*Pinus sylvestris* L.) sapwood and from heat treated Norway spruce (*Picea abies* K.). The acetylation was performed according to Rowell *et al.* (1986), the wood acetyl content was about 20%. The heat treatment was performed by Stora Enso according to the ThermoWood® D procedure. All boards were ground into particles in a two step process by means of a disk flaker and a dry grinding knife mill. The thermoplastic matrix used was polypropylene (PP, Moplen HF 500N). The wood components were dried to a moisture content (MC) of less than 1% and compounded together with the PP into pellets at OFK Plast AB. The wood/PP ratio was 70/30 based on dry weight. The pellets were then fed into a conical extruder located at Conenor Oy, and extruded into rectangular-shaped hollow profiles with a cross section measuring 60 x 40 mm² with a wall thickness of 8 mm. Thin specimens were cut out from the profiles according to Figure 1.

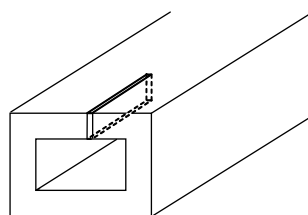


Figure 1: Schematic drawing of the type of specimens sawn out of the hollow WPC profiles

The specimens measured 40 x 1.8 mm² and the width corresponded to the original thickness of the hollow profile (ca 8 mm). One set of matching specimens were then oven-dried and exclusively used to determine the initial moisture content of the composites. The initial dimensions and weight were recorded for the rest of the specimens prior to immersion in de-ionized water kept in closed jars. All immersed specimens were weighed after three weeks and then immersed again and left for three years before the test was terminated and the final moisture and dimensional changes were recorded. The specimens were washed and wiped of excess water before the weight and dimensions measurements. The results from the moisture soaking experiments were then used to try to determine the cell wall density as well as the porosity in the composites. The assumptions made are that the fibre saturation point is 30%, 20% and 10% for the unmodified, heat treated and acetylated wood component respectively. As well as that all voids are filled with water for the saturated specimens.

RESULTS AND DISCUSSION

Table 1 presents the starting and final moisture content (MC) of the water immersed WPC samples, both for the total WPC, and by excluding the polypropylene (PP) matrix. Since this matrix material do not absorb any moisture, the latter value is more representing the actual MC in the wood component including also the moisture in any voids. As can be seen, and as expected, the WPC samples containing a modified wood component gained significantly less moisture compared with the samples with unmodified wood. It can also be noticed that the final MC of the WPCs with unmodified wood, excluding the PP matrix, reached a MC content higher than a normal fibre saturation point (FSP) for pine wood, indicating that this material has a porosity and/or that voids have been formed within the material, perhaps due to swelling stresses. A similar observation can be made for the composites with a modified wood component, if it is assumed that the FSP of the acetylated wood is ca 10% and for the heat treated wood ca 20 %, based on reported water vapour sorption values at high humidity levels for similar materials (Segerholm 2007). I should also be noted that all of the WPCs had reached saturation already after three weeks immersion. At this stage it was also observed some supposedly algae growth on the samples with untreated and heat treated wood. No or very little of such algae growth could be observed on the samples containing an acetylated wood component even after three years of water immersion.

Table 1: Start and final moisture content (MC) of the WPC samples. Based on 5 replicates, standard deviation in parentheses.

WPC sample	MC [%] of the total WPC		MC [%] of the WPC excluding the PP matrix	
	Start	Final [%]	Start	Final
Unmodified Axial long	3.2 (0.2)	28.6 (0.3)	4.6 (0.3)	40.9 (0.5)
Acetylated Axial long	1.4 (0.2)	10.3 (0.2)	2.0 (0.3)	14.6 (0.2)
Heat treated Axial long	2.5 (0.1)	19.9 (0.4)	3.6 (0.2)	28.5 (0.6)

Table 2: Swelling of the WPC materials due to water soaking. Based on five replicates. Standard deviation was 0.1–0.3% for the length and width directions and 0.5–1.3% for the thickness direction.

WPC sample	Swelling [%]		
	Length	Thickness	Width
Unmodified	1.9	11.1	9.6
Acetylated	0.3	3.2	1.7
Heat treated	1.4	5.2	6.3

Table 2 presents the corresponding dimensional changes of the water immersed WPC samples. As can be seen the resulting swelling is significantly lower for samples containing modified wood as compared with the controls. There is also a notable higher swelling transverse the extrusion direction. The porosity of WPCs is generally in the range of 2–10%, i.e. very low compared to most wood species. By applying the rule of mixture for the densities of the different WPC components and assuming that all voids are filled with water at saturation, combined with the over-all densities of the WPCs in their dry and saturated state, as presented in Table 3, indicates a dry wood cell-wall density for the unmodified, acetylated and heat treated wood component as presented in table 4. Such an estimation should, however, be verified by more accurate measurements of the modified wood cell walls.

Table 3: Estimation of the density of the WPC samples, before (Start) and after soaking (Final). Based on 5 replicates. Standard deviation was 0.01 g/cm³ for all samples.

	WPC density [g/cm ³],		
	Unmodified	Acetylated	Heat treated
Start	1.19	1.15	1.19
Final	1.16	1.17	1.19

Table 4: Estimations of the cell wall densities for the unmodified, acetylated and heat treated wood components

Material	Measured density	Moisture content	PP + additive		Wood component		Bound water in the cell-wall ¹		Pores ²		Cell-wall density ³
	[g/cm ³]	[%]	W-%	Vol.-%	W-%	Vol.-%	W-%	Vol.-%	W-%	Vol.-%	[g/cm ³]
WPC with untreated wood											
In-door conditioned	1,19 (0,1)	3,2 (0,2)	29,1	38,0	67,8	56,8	3,1	3,7	0	1,5	1,42
Water saturated	1,16 (0,1)	28,6 (0,2)	23,3	29,7	54,4	44,5	16,3	18,9	5,9	6,9	1,42
WPC with acetylated wood											
In-door conditioned	1,15 (0,1)	1,4 (0,2)	29,6	37,4	69,0	57,9	1,4	1,6	0	3,2	1,37
Water saturated	1,17 (0,1)	10,3 (0,2)	27,2	35,0	63,5	54,1	6,3	7,4	3,0	3,5	1,37
WPC with heat treated wood											
In-door conditioned	1,19 (0,1)	2,5 (0,1)	29,3	38,3	68,3	55,6	2,4	2,9	0	3,2	1,46
Water saturated	1,19 (0,1)	19,9 (0,2)	25,0	32,7	58,3	47,5	11,7	13,9	5,0	5,9	1,46

¹Assuming a fiber saturation point of 30% for untreated wood, 10% for acetylated wood, and 20% for heat treated wood

²Filled with water for the saturated WPCs

³Based on the rule of mixture. Cell wall density is calculated for the water saturated specimens, assuming that all pores are saturated with water

CONCLUSIONS

Modified wood used in WPCs can greatly reduce the water sensitivity and resulting dimensional changes for high wood content WPCs. Thin sections (1.8 mm thick) of WPCs can reach fibre saturation after three weeks water soaking.

ACKNOWLEDGEMENTS

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Soft Rot Decay of Polypropylene/Acetylated Fibre Composites

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Keywords: Polypropylene/acetylated wood fibre composites; acetylation; bioresistance

ABSTRACT

Influence of wood fibre acetylation and percentage of polypropylene grafted maleic anhydride compatibilizer (MAPP) on bioresistance of the polypropylene/acetylated wood fibre composites against the soft rot decay was the main concern of this study. Wood fibres were acetylated to achieve weight gains of 0, 4.5, 7.5 and 17.6% by using acetic anhydride. The acetylated fibres (60%^{w/w}) were mixed with the MAPP (with percentages of 0, 2, 3 and 5%^{w/w}) and polypropylene (40%^{w/w}). The mixture was moulded in a hot press to prepare samples of the acetylated wood plastic composites (WPCs). Samples in sizes of 2×10×100mm were cut, dried and weighed before exposing to soil bed according to ENV 807. Mass losses and moisture contents of the WPCs were determined after 4 and 6 months of the exposure to the soil bed. Results revealed that the acetylation increased the bioresistance of the WPCs against the soft rot fungi. Mass loss of the WPCs was reduced as the weight gain increased in the samples. Moisture content of the samples was also decreased due to the acetylation. Increase of the MAPP reduced the mass loss in the untreated samples as well as the acetylated composites with a weight gain of 4.5%. However, the MAPP had no significant effect on the mass loss and moisture absorption of the acetylated WPCs during the fungal attack.

INTRODUCTION

The WPCs are composed of the wood as filler, plastic polymers as matrix and compatibilizers, which are responsible to bond both phases of the wood and the polymers to each other. The matrix polymers are hydrophobic and bioresistant and they encapsulate wood phase in the WPCs. For these reasons, it is believed that the WPCs are bioresistant and hydrophobic materials (Stark 2001) and the fungi as well as the water molecules are not able to access the hydrophilic and biodegradable wood phase in the WPCs. Wood forms a polar phase and the plastic forms a non-polar phase of the WPCs. As there is no appropriate compatibility between both phases due to different polarities; the compatibilizers are used to improve coupling between the wood and the plastic polymers (Chowdhury and Wolcott 2007). Improvement of the interfacial bonding affects properties of the WPCs and reduces voids and gaps between interfaces of the wood and the plastics. The hydrophobic matrix polymer is able to protect the hydrophilic and biodegradable wood phase from access of the water molecules as well as the microbial attacks. However, new research reports criticize the previous beliefs. As it has been indicated the wood plastic composites are susceptible to fungal attack and they are capable of moisture absorption in long term of services (Adhikary *et al.* 2008). Concerning the reports, the wood phase in the WPCs remains susceptible to fungal attack and hydrophilic. There is a conceptual idea that any alteration in the chemistry of the wood phase from hydrophilic to hydrophobic, increase of its moisture repellency as well as the bioresistance, might affect the properties of the WPCs. Only few reports have concerned the idea of modifying the lignocellulosic portion of the WPCs.

Application of the modified wood in the WPCs showed inhibitory effect of the wood modification on fungal activities (Ibach and Clemons 2002, 2006, Ibach *et al.* 2007, Schirp *et al.* 2008). Galland (2009) studied microstructure and micromechanics of chemically and thermally modified wood plastic composites. He showed proper compatibilization between modified wood and the matrix polymer HDPE. This research has intended to study influence of the modifying aspect of the wood fibre acetylation on bioresistance of the WPCs and compare its effect with the typical compatibilizer MAPP.

EXPERIMENTAL

Acetylation- MDF fibres were oven dried at $103\pm 2^\circ\text{C}$ for 24h. Afterwards, acetylation reaction was carried out in a stainless steel reactor by using acetic anhydride at 120°C with no catalyst to achieve weight gains (WPGs) of 0, 4.5, 7.5 and 17.68%.

Manufacture of wood plastic composites- Wood fibres (acetylated and non-acetylated) as 60%, polypropylene (PP) (45-50%) and polypropylene grafted maleic anhydride (MAPP) (0-5%) were mixed in a Brabender (PLASTI-CORDER model) at 30 rpm and 180°C . to mould in a hot press at 180°C for 8min.

Soil bed trial- Soil boxes were prepared according to standard ENV 807 and the test samples were planted in the soil and kept at

Water holding capacity (WHC) of the soil was determined according to the standard method and then soil moisture was adjusted to 95% of the WHC. Mini-stakes of $2\times 10\times 100\text{mm}$ were cut from main samples of the WPCs, weighed before and after the oven drying at $103\pm 2^\circ\text{C}$ for 24h to determine the moisture contents.

For each prepared WPCs, 10 mini-stakes were randomly planted into the soil vertically with about 20mm distances from each side. Also, 20mm of the mini-stakes was protruding above the soil surface and 80mm into the soil. The prepared soil beds were kept at a controlled condition (temp $26\pm 1^\circ\text{C}$ and RH $65\pm 5\%$) for 6 months. Sampling was carried out after 6 months to determine mass losses in the WPCs. The samples were weighed before and after oven drying to determine the moisture contents as well as the mass losses.

RESULTS AND DISCUSSION

Results revealed that increase of the WPGs reduced significantly the mass loss in the acetylated WPCs for all percentages of the compatibilizer after exposure to the soil bed (Fig. 1). The high the weight loss was determined in the non-acetylated WPCs with no compatibilizer (MAPP); while, application of the MAPP reduced slightly the mass loss; especially in the non-acetylated samples. It seems, there was no inhibitory effect of the compatibilizer. In the acetylated composites, increase of the WPGs dominated the significant effect of the MAPP on soft rot decay. As it has shown, no significant variation of the mass loss due to increase of the MAPP was determined in the acetylated WPCs with the weight gain of 17.6%; while any increase of the MAPP reduced the mass loss in the non-acetylated as well as the acetylated composites at the WPG of 4.5%. Moisture contents (MC) of the WPCs was affected by the acetylation (Fig. 2). It is likely that, the moisture content of the WPCs is due to fungal metabolic activities as well as absorption from the wet soil. Increase of the WPGs reduced significantly the MCs in the composites. Concerning the results, the non-acetylated composites could achieve the highest amounts of the moisture contents even for all percentages of the MAPP. Increase of the WPGs dominated the effect of the MAPP in all applied percentages; especially in the composites with a weight gain of 17.68%.

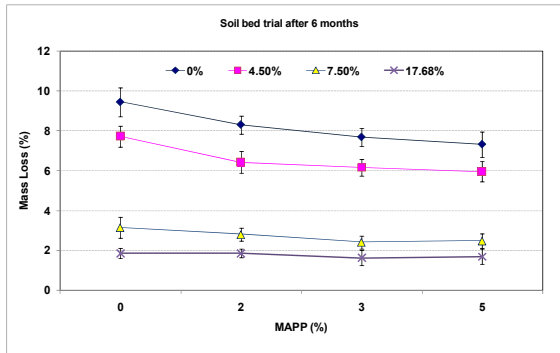


Figure 1: Mass loss in soft rot decayed WPCs

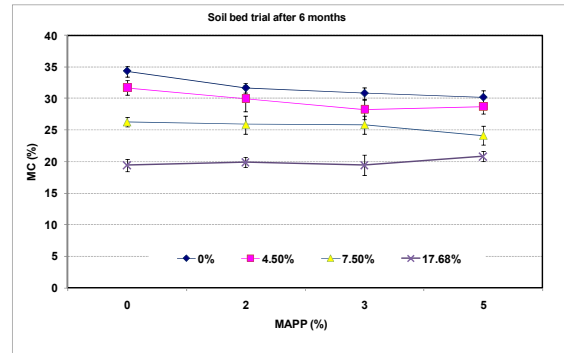


Figure 2: Moisture absorption in soft rot decayed WPCs

It is well known that the polypropylene is a hydrophobic polymer. Therefore, any moisture absorption in the WPCs is occurred due to hydrophilic fraction; such as the cellulose and the hemicelluloses. It was an assumption that any alteration in the hydrophilicity of those polymers due to the acetylation might affect the properties of the WPCs. Correlation between the mass losses of the WPCs and the moisture contents due to the microbial activities has shown in Fig. 3. Results revealed that the mass loss in the WPCs is highly correlated with the moisture contents. Any increase in the moisture contents is a consequence of the mass loss in the wood plastic composites. However, the acetylation reduced the moisture content as well as the mass losses in the composites. Any increase of the WPGs decreased significantly the moisture contents as well the mass losses due to activities of the soil microorganisms. Concerning the results, there was no significant differences between the composites with and without the compatibilizer MAPP. Application of the MAPP could not affect the mass loss or the moisture contents in the WPCs; especially in the acetylated composites (Fig. 3).

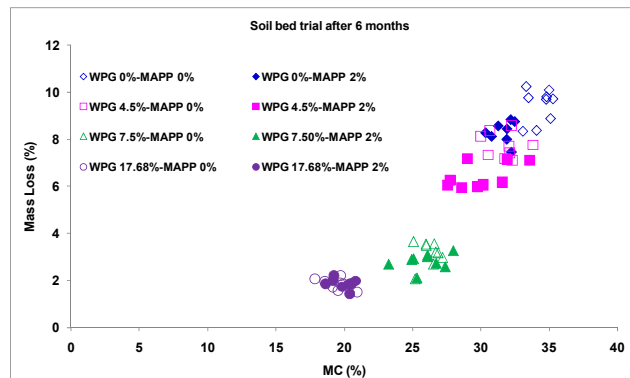


Figure 3: Correlation between mass loss and moisture contents of WPCs

The MAPP as a compatibilizer and performs two different roles in the composites; a) providing better encapsulation of the lignocellulosic part of the WPCs by the matrix polymer PP, and b) reduction in the void volumes by removing the interfaces between both phases; the wood and the polymers. Both aspects of the MAPP could decrease access of the water molecules and the fungal hyphae to the hygroscopic biodegradable wood or fibre in the WPCs. It is likely that, increase of the MAPP performed both aspects in the non-acetylated WPCs. It reduced the mass losses due to soil microbial activities as well as prohibition in access of the fungal metabolic moisture to the encapsulated hydrophilic fibres by polypropylene. Application of the MAPP causes ester bonds in the wood polymers by blocking the hydroxyl groups and changing their chemistry to hydrophobic (Yang *et al.* 2007). In the acetylated WPCs, influence of the MAPP was dominated by the acetylation. During the acetylation reaction, substitution of the hydroxyl groups by the acetyl groups altered the cell wall chemistry of the wood

phase and changed it to a hydrophobic and moisture repellent material (Mohebbi and Hadjihassani 2008). According to Dominkovics *et al.* (2007) chemical modification of the wood flour decreases the surface tension of the composites. Due to the altered chemistry of the wood, microorganisms are not able to recognize the cell wall polymers and they are not able to react with the water molecules due to reduced surface tension.

CONCLUSIONS

Following results can be withdrawn from the current research work: 1) Influence of the MAPP application is prominent in the non-acetylated WPCs. The MAPP could reduce the microbial activities and moisture contents. However, acetylation of the fibres dominates the performance of the MAPP and it can also significantly reduce the mass loss and moisture contents in the WPCs. 2) Increase of the MAPP has no significant influence on the soil microbial activities in the acetylated composites; while any increase in the weight percent gains of the fibre can prohibits the microbial activities in the composites.

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Absorption and Diffusion of Water in Acetylated Fibre/Polypropylene Composites

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Keywords: Wood plastic composites, acetylation, compatibilizer MAPP, water absorption, water diffusion

ABSTRACT

Long term water absorption of acetylated fibre/polypropylene composites (WPCs) was concerned in this work to study the water diffusion. Wood fibres were acetylated to achieve weight percent gains (WPGs) of 4.5, 7.5 and 17.68%. The acetylated fibres were mixed with the MAPP to manufacture the WPCs by moulding under a hot press. Test samples were cut and soaked in the water for 1512 hours at room temperature to determine the water absorption as well as the water diffusion in the composites. Results revealed that application of the acetylated fibres reduced the water absorption and the sorption maxima in the wood plastic composites. Also, the acetylation extended the sorption time and retarded the water diffusion into the WPCs. Application of the MAPP showed similar results as the acetylation. However, the influence of the acetylation was more prominent than the compatibilizer.

INTRODUCTION

Within the recent years, most of the research works have concerned application of the wood/lignocellulosic fibres as natural fillers in the wood plastic composites (WPCs). The natural fibres are interested due to low densities, low processing costs, regeneration (Mechraoui *et al.* 2007). The WPCs are composed of two different phases, fibre and plastic polymers. Incompatibility between both phases is major problem in production of the WPCs (Espert *et al.* 2004, Mechraoui *et al.* 2007). Different types of the compatibilizers are used to improve interfacial bonding between the wood and the plastic matrix polymers. Properties of the WPCs are affected by the interfaces between both phases, such as mechanical strengths, moisture absorption as well as the water absorption. Applications of the WPCs are defined by their properties. The wood plastic composites are used in critical positions as building materials, such as flooring, outdoors, door and window frames, sauna, etc. Regarding the places where the WPCs are used, water/moisture absorption properties are very important (Kazemi-Najafi *et al.* 2007), because, the mechanical strengths as well as dimensional stability of the WPCs are affected by the water absorption (Tajvidi *et al.* 2006, Adhikary *et al.* 2008). Polymeric structure of the wood is main reason of the hygroscopic behaviour of the WPCs, because the main portion includes the wood or lignocellulosic fibres, which bind with the water molecules via the hydrogen bonds.

There are numerous research reports that concern surface treatment of the wood fibres to reduce the hygroscopicity (Demir *et al.* 2006, Tserki *et al.* 2005). Modification of the lignocellulosic portion is an assumption to alter the chemistry of the wood polymers to hydrophobic in the WPCs. Acetylation is a well known technique of the chemical wood modification which increases dimensional stability, bioresistance, photostability of the wood (Rowell 2006, Ibach and Clemons 2002&2006, Mohebbi and Hajhassani 2008).

There are few reports that indicate application of the acetylated wood fibres in the wood plastic composites (Ibach and Clemons 2007). Those reports are dealing with increase of the bioresistance.

Water diffusion coefficient is an important parameter to interpret the absorption behaviour of the WPCs. Diffusion coefficient of the water is theoretically obtained from sorption slope according to equation 1 (Shi and Gardner 2006).

$$Kt^n = M_t/M_\infty \quad (1)$$

where, M_t represents absorbed water at time t (%), M_∞ , maximum water absorption (%) and K (h^2) and n are constants.

The Fickian theory is used to analyze the water absorption in the composites. The empirical equation 2 is used to predict the data.

$$\text{Log}(M_t/M_\infty) = \text{Log}(k) + n \text{Log}(t) \quad (2)$$

The water diffusion coefficient indicates capable penetration of the water molecules into the composites' structure. "n" is obtained from equation 2. For the composites "n" is less than 0.5. It is used to calculate M_t/M_∞ according to equation 3 (Espert *et al.*, 2004).

$$M_t/M_\infty = (4/L) \cdot (D/\pi)^{0.5} t^{0.5} \quad (3)$$

where, D represents water diffusion (m^2/s).

Mechanism of the water diffusion in the acetylated WPCs is still unknown. As it was mentioned above, the major portion of the WPCs is the wood and lignocellulosic materials. In untreated wood plastic composites, the natural feature of the wood portion is still unchanged after production. Therefore, swelling of the composites will be expected when the water access this portion. Therefore, properties of the WPCs will be affected due to the water absorption. This research is attending to study the water absorption behaviour in the acetylated WPCs and compare the influence of the acetylation with the compatibilizer MAPP.

EXPERIMENTAL

The wood fibres were reacted with acetic anhydride at temperature 120°C to achieve weight percent gains (WPGs) of 4.5, 7.5 and 17.68%. The acetylated fibres (60% w/w) were mixed with matrix polymer polypropylene (PP 38% w/w, grade SI-080, melt flow index, $9^g/10\text{min}$) and maleated polypropylene (MAPP 2% w/w) as compatibilizer in a Brabender Plasticorder and moulded ($2 \times 150 \times 150\text{mm}$) in a hot press at 180°C based on a target density of 1g/cm^3 . Test samples ($2 \times 20 \times 20\text{mm}$) were cut, oven dried and soaked in water for 1512 hours at room temperature. Wet weight of the samples was measured versus the soaking time to determine the maximum water absorption and water diffusion according to equations 1 to 3.

RESULTS AND DISCUSSION

Results revealed that acetylation of the fibres and application of the MAPP reduced the water absorption of the WPCs (Fig. 1). Reducing effect of the MAPP was prominent in the non-acetylated WPCs than that of the acetylated one. According to the results, the experimental data of the water absorption adopted with predicted one in both types of WPCs (Fig. 2). The coefficient "n" is an indication of the water diffusion behavior in the composites. This coefficient is an indication of the water flow in the composites. For the cases in which the coefficient is $n \leq 0.5$, the water diffusion follows Fickian theory (Shi and Gardner 2006). According to the results the amount of "n" is less than 0.5 in the WPCs (Table 1). It means that the diffusion of the water follows the Fickian model in the acetylated WPCs.

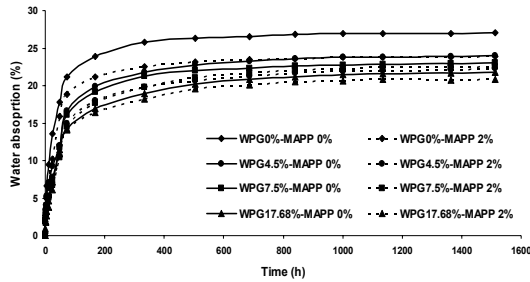


Figure 1: Long term water absorption in acetylated WPCs

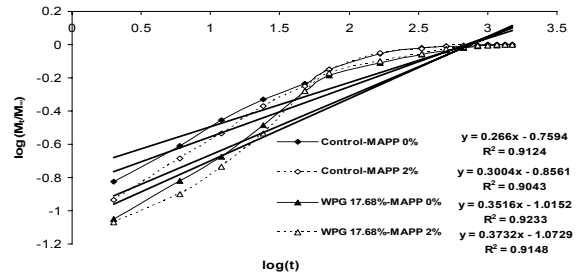


Figure 2: Fitted lines of water absorption in acetylated WPCs

The “k” is sorption time of a composite. When the time is shortened, the material is saturated by water in a shorter period (Kazemi-Najafi *et al.* 2008). In table 1, results indicate that “k” is reduced by the acetylation. The acetylated fibres are water repellent and would not bind with the water molecules due to hydrophobicity (Mohebbi and Hadjassani 2008). Also, the compatibilizer MAPP reduced the void volume in the composites. It could be expressed that reduction of voids in the WPCs as well as application of the hydrophobic fibres are the reasons for decrease in water absorption and sorption time. Study on the sorption behavior of the WPCs showed that the acetylation as well as the compatibilizer reduced the water absorption maxima and the sorption time (Table 1). Reduction in sorption maxima indicates that the acetylated composites had lower capacity to keep the water inside. Increase of sorption time indicated that the acetylated composites required a longer time to achieve the sorption maxima. It means that the acetylated WPCs are highly water repellent and able to resist in very humid or wet conditions. Reduction in the water diffusion of the WPCs also confirmed these results (Table 1).

Table 1 Parameters of water diffusion in acetylated WPCs

Formulation	n	K (h ²)	Sorption maxima (%)	Sorption time (h)	Water diffusion coefficient (×10 ⁻¹² m/s ²)
WPG 0-MAPP 0%	0.4527	0.1062	27.0	540	2.0
WPG 0 -MAPP 2%	0.4947	0.0825	23.8	540	1.6
WPG 4.5%-MAPP 0%	0.4532	0.0941	24.0	840	1.6
WPG 4.5% -MAPP 2%	0.4934	0.0913	23.7	1134	1.4
WPG 7.5%-MAPP 0%	0.4595	0.0836	23.0	1134	1.5
WPG 7.5% -MAPP 2%	0.4454	0.0821	22.5	1134	1.3
WPG 17.68%-MAPP 0%	0.4996	0.0502	21.7	1134	1.3
WPG 17.68%-MAPP 2%	0.4871	0.0417	20.7	1134	1.3

The results here showed that the acetylation of the fibres reduced the water absorption and sorption maxima in the WPCs. Also it increased the sorption time and reduced the diffusion coefficient. Application of the MAPP had similar influence on properties of the WPCs. However, the influences of the acetylation were more prominent than the MAPP. Acetylation reaction changes the fibres to hydrophobic and water repellent materials (Mohebbi and Hadjassani 2008, Ibach *et al.* 2007). The compatibilizer MAPP improves the interfacial bonding between the matrix polymer and the fibres (Adhikary *et al.* 2008). Consequence of MAPP application is reduction in the voids volume of the WPCs (Shi and Gardner 2006, Yang *et al.* 2007, Demir *et al.* 2006). Therefore, it can be expressed that the acetylated WPCs have lower capacity of the water absorption due to increased water repellency of the acetylation. Improvement of the interfacial bonding and decrease of the voids are the reason for longer diffusion time and lesser sorption maxima.

CONCLUSIONS

Regarding the results above, it could be expressed that reduction in the water absorption, the water diffusion coefficient, sorption maxima as well as increase of the saturation time are results of the fibre acetylation and application of the MAPP. Sorption and diffusion properties of the acetylated WPCs adapted to Fickian’s theory.

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Hygrothermal Pre-treatment of Strands: Effects on Technological Properties of OSB Made from a Mixture of Eucalypt and Pine Species

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Keywords: Biological properties, dimensional stability, hygrothermal treatment, mechanical properties.

ABSTRACT

This paper aims at evaluating the effect of a hygrothermal treatment of the strands on the technological properties of oriented strandboard (OSB) made from a mixture of eucalypt and pine species. Strands from *Eucalyptus urophylla* and *Pinus taeda* were hygrothermally treated using an autoclave (120°C; 1.0 N/mm²) for 15, 30 and 60 minutes. Untreated strands were kept as control treatment. For each treatment three three-layer (25:50:25) boards were produced using a mixture of *E. urophylla* (16.4% w/w) and *P. taeda* (83.7% w/w). The boards were manufactured according to the following characteristics and procedures: board dimensions about 450 x 450 x 12.5 mm³ (*l* x *w* x *t*), target density 0.65 g/cm³, 8% of phenol-formaldehyde resin, pressing temperature 190°C for 8 minutes (4.0 N/mm² specific pressure). According to the results, the hygrothermal pre-treatment did not have any positive effect on the dimensional stability of the board in comparison with untreated boards. On the other hand, the evaluated pre-treatment improved slightly the compression strength (60'), the modulus of elasticity and the internal bonding (30' and 60'). Regarding biological properties, the evaluated pre-treatment had a positive effect against white-rot fungus, but was ineffective against brown-rot fungus. Finally, although the evaluated mild hygrothermal pre-treatment did not improve the dimensional stability of the boards, it did not imply any adverse effect on the mechanical properties either. It is an interesting finding, since thermally pre-treated furnish usually implies losing strength of the board.

INTRODUCTION

In the last four years several researches have been done regarding improvement in the performance of wood based products (Çavdar *et al.* 2010, Del Menezzi *et al.* 2009, Mohebbi *et al.* 2008, Del Menezzi *et al.* 2008, Okino *et al.* 2007, Paul *et al.* 2007, Paul *et al.* 2006). The main concern is about the development of methods leading to better dimensional stability of panel products made from particles, strands, or fibers. Most of these methods comprise thermal modification of either furnish or the consolidated panel. For the latter, the consolidated board is heated again under dry or wet conditions, and then the compression stresses can be released, significantly reducing thickness swelling. On the other hand, for the first group of method, the furnish is thermally pre-treated and afterwards the panel is manufactured. In this case, methods can be simply classified as

hygrothermal (under steam) or hydrothermal (in water), as defined by Hill (2006). According to Sekino *et al.* (1999), when furnish is thermally pre-treated it becomes more compressible, reducing remaining latent compression stresses into the board after the hot-pressing stage. Thus, when the board gets in contact with water, thickness swelling due to releasing of compression stresses can be lower. Some thermal degradation of furnish is also expected to happen, leading to a reduction of its higroscopicity. Nevertheless, if severe pre-treatment is applied it can impair the bonding process, thus reducing significantly the mechanical properties of the board, as observed by Mohebbi *et al.* (2008), Paul *et al.* (2007) and Paul *et al.* (2006). In this context, the present paper aimed at studying the effect of a mild hygrothermal pre-treatment on the properties of laboratory-made oriented strandboards (OSB).

EXPERIMENTAL

Strands from *Eucalyptus urophylla* and *Pinus taeda* were produced, dried and stored in a conditioning room (65% RH; 20°C). Afterwards, the strands were hygrothermally treated using an autoclave (120°C; 1.0 N/mm²) for 15, 30 and 60 minutes. Untreated strands were kept as control treatment. For each treatment three three-layer (25:50:25) boards were produced using a mixture of *E. urophylla* (16.4% w/w) and *P. taeda* (83.7% w/w). The boards were manufactured according to the following characteristics and procedures: board dimensions about 450 x 450 x 12.5 mm³ (*l* x *w* x *t*), target density 0.65 g/cm³, 8% of phenol-formaldehyde resin, pressing temperature 190°C for 8 minutes (4.0 N/mm² specific pressure). Physical (water absorption-WA, thickness swelling-TS and permanent thickness swelling-PTS) and mechanical properties (modulus of rupture-MOR, modulus of elasticity-MOE, maximum load-ML, internal bonding-IB and compression strength-CS) were determined according to ASTM D1037. Additionally, biological resistance tests against brown-rot (*Gloeophyllum trabeum*-WL-GT) and white-rot (*Trametes versicolor*-WL-TV) fungi were conducted according to ASTM D2017. For each test, 2 samples per board were taken. The data obtained were initially analysed by running an analysis of variance (ANOVA) and then Tukey HSD mean tests were run to separate treatment means.

RESULTS AND DISCUSSION

Table 1 presents the results of physical, mechanical and biological properties of the evaluated treatment. It can be observed that the properties related to dimensional stability (WA, TS and PTS) were not affected by the hygrothermal treatment applied. On the other hand, the mechanical properties MOE, IB and CS could be slightly improved as treatment duration was extended. For the biological property, the same behaviour was observed. Thus, an improvement in biological resistance against white-rot fungus *T. versicolor* could be achieved. In this context, according to the results obtained, the applied hygrothermal treatment did not improve dimensional stability, but it did not affect adversely the mechanical properties either, which has been often found as a side effect of the furnish pre-treatments. These findings partially differ from those obtained by other authors. Mohebbi *et al.* (2008) pre-treated fibres, achieving a significant improvement in TS, but WA was not affected by the pre-treatment applied. Paul *et al.* (2006) pre-treated strands of *Pinus sylvestris* at 220 and 240°C for 30 minutes. All dimensional stability properties were enhanced, conversely to bending properties and IB. They also achieved an enhancement of durability against brown-rot fungus *Poria placenta* (Paul *et al.* 2007). Jones *et al.* (1999) observed that thickness

swelling of binderless fiberboard was significantly reduced as treatment was applied at a higher temperature for a longer period of time. Surely, the source of these variations is the conditions of the treatment, such as: moisture content of furnish, pressure, temperature, closed or open system, steam or water, etc. Theoretically, pre-treatment improves furnish compressibility by reducing internal stresses and promoting polymer chemical degradation. Consequently, boards made from pre-treated strands were expected to present better dimensional stability; however they did not.

Table 1: Physical, mechanical and biological properties of OSB made from untreated and hygrothermally pre-treated strands.

Property	F	Untreated	15 [min]	30 [min]	60 [min]
WA2h (%)	1.563 ^{NS}	50.9	55.2	45.0	46.4
WA24h (%)	1.266 ^{NS}	64.1	68.4	58.3	59.9
TS2h (%)	1.237 ^{NS}	16.6	19.9	17.7	17.5
TS24h (%)	0.816 ^{NS}	22.6	25.6	22.9	24.0
PTS (%)	1.921 ^{NS}	14.6	18.1	14.7	15.9
MOR// (MPa)	0.294 ^{NS}	32.7	33.1	31.8	34.8
MOE// (MPa)	7.521**	5181.2a	5622.8a	5847.9ab	6000.3b
ML (N)	0.299 ^{NS}	998.7	940.0	902.8	988.7
IB (MPa)	5.984**	0.34a	0.34a	0.44b	0.43b
CS (MPa)	4.221*	13.0a	12.0a	10.9a	15.7b
WL-TV (%)	6.111**	18.7a	25.1a	13.1b	16.9ab
WL-GT (%)	1.729 ^{NS}	19.8	28.9	18.5	23.2

^{NS} non-significant *, ** significant at $\alpha=0.05$ and $\alpha=0.01$, respectively

It can be speculated that temperature or duration of treatment was not enough to degrade considerably the chemical polymers. However, Hsu *et al.* (1988) obtained very interesting results for dimensional stability using short treatment (less than 5 minutes at 1.55 N/mm²). According to Jones *et al.* (1999) hygrothermal treatment refers to the application of high temperature steam under pressurised conditions. Although the temperature and duration of this kind of pre-treatment can vary, the range is usually above 150°C for longer periods of time. Nevertheless, the conditions of the applied hygrothermal treatment might have entailed some chemical degradation, since a slight enhancement of the biological resistance could be achieved. As well-known, the less thermally stable polymer is hemicelluloses, being firstly degraded, which reduces the fungus feeding, as observed by Del Menezzi *et al.* (2008). The steam applied during the treatment might have cleaned the strand surface, thus removing extractives and resin drops, promoting better conditions for resin polymerization, and eventually enhancing IB strength. Furthermore, MOE and CS benefited from this enhancement and their values were slightly higher than those from untreated boards. The relationship between these properties is discussed by Del Menezzi *et al.* (2009).

CONCLUSIONS

Although the evaluated mild hygrothermal pre-treatment did not improve the dimensional stability of the boards, it did not imply any adverse effect on mechanical properties either. It is an interesting finding, since thermally pre-treated furnish usually implies losing strength of the board. Additionally, some improvement of biological resistance against white-rot fungus was also observed. Thus, this research project will be continued in order to clarify or even improve the results obtained.

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Modified Grey Alder Wood – an Excellent Raw Material for Production of High Density and Strength Activated Carbon

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Keywords: Activated carbon, carbonization, hydrothermal pretreatment, lignocellulosic sources, pelletization.

ABSTRACT

Biomass is currently a promising renewable and potentially neutral raw material in relation to global warming. Modified and pelletized fast-growing grey alder (*Alnus incana*) wood was used as precursor for activated carbon preparation by physical activation with superheated steam under a self-generated atmosphere. The impact of the relative moisture content before pelletization in the range 4-12% on the mechanical properties of pellets and on the developed porous structure of the obtained carbons were studied for 90 min of activation time at the 850°C of temperature. Modified grey alder wood was treated for 2 h at 180°C and obtained pellets mechanical properties as well as surface properties of the activated carbons were dependent on a combined effect of the conditions employed. As optimal carbonization temperature selected 600°C, because the prepared activated carbons characterize with the highest bulk density, yield and micropore content from the total pore volume.

INTRODUCTION

Due to the global environmental concerns for the excessive use of fossil fuel, sustainable biomass resources have grown in importance as partial alternatives to fossil resources. More and more terms such as “green energy”, “green products” and “sustainable development” emerge. One of the ways is to produce “green products” employing environmentally friendly technologies. Wood is the main renewable resource available in Europe; therefore, this is the raw material, which has been examined thoroughly trying to process this excellent material and obtain products with a high added value. Granular activated carbon (GAC) meets this condition. To meet the increasing demand for activated carbon (AC), it is necessary to develop and efficiently realize innovative technologies of its obtaining. The aim of activation is to obtain a high-porosity and internal surface area. Physical activation has been chosen corresponding to the environmentally friendly technology (Toles *et al.*, 2000). The adsorbents prepared by steam activation have a microporous structure, which satisfies the criteria of gas phase adsorbents. AC can be prepared from a variety of raw materials. The most frequently used precursors for ACs are wood and its residues (Amaya *et al.*, 2007), nut shells, fruit stones and agriculture residues (Gergova *et al.*, 1994). A raw material with a high bulk density and a low content of volatiles such as nut shells and fruit stones is appropriate to produce mechanically strong GAC with a high adsorption capacity. In North Europe, however, these raw materials are either non-available or available in insufficient amounts. Therefore, it is proposed in this study to obtain mechanically strong GAC from modified and pelletized grey alder (GA) wood. Grey alder (*Alnus incana* (L) Moench) wood as a raw material for production of AC is very

appreciative, because it is an excellent pioneer species for re-establishing woodlands on disused farmlands. Also due to the high content of hemicelluloses (26.9 wt%), GA wood is a promising raw material for hydrothermal modification under pressure for further pelletization, carbonization and steam activation to prepare dense and mechanically strong GAC. The hydrothermal treatment process is also called autohydrolysis, because the reaction is catalyzed by the hydronium ions from the autoionization of the water and acetic acid released from hemicelluloses by the cleavage of acetyl side chains, and the weak acidic environment created thereby is sufficient to promote the hydrolysis of the rest of hemicelluloses. As a result, free sugars are reactive and can be decomposed under heat into furfural and other decomposition products, which can be further transformed into a polymeric substance to provide a bounding and bulking effect on the obtained lignocellulosic material by the application of heat and pressure in a pelleting operation, resulting in composite products with a good mechanical strength and an excellent dimensional stability. The obtained modified wood (MW) contains from 10 to 30% of water-soluble matter (Rizhikovs *et al.*, 2009); therefore, water acts as both a binding agent and a lubricant. Water helps in developing Van der Waals' forces by increasing the area of contact between the particles. Several studies have shown that the strength and durability of densified materials increase with increasing moisture content until an optimum is reached, and good quality wood pellets can be produced with initial moisture contents of 6-12 wt% (Li and Liu, 2000). For MW, however, the optimal moisture must be determined to obtain dense and mechanically strong pellets. It is very important to retain the mechanical properties of the pellets also after carbonization and activation. Therefore, the effect of the moisture content before pelletization on the adsorption and mechanical properties of steam AC was investigated.

EXPERIMENTAL

The technology for the production of granular activated carbon from MW consists of the following steps:

- Drying of wood chips for further milling;
- Hydrothermal pretreatment of chipped GA wood;
- Milling of dry MW chips for further pelletizing;
- Pelletizing of dry MW;
- Carbonization and activation of pelletized MW.

Sample preparation

Freshly cut GA wood chips, after drying at room temperature to the moisture content 10-15% on the wet mass basis, were used for further operations. Five variants of the initial moisture content before pelletization were prepared to study the impact of water on the mechanical properties of MW pellets, carbonized pellets and GAC. The initial moisture content necessary for the experiments was achieved, mixing the MW with the fractional composition below 2 mm with the calculated water amount and holding in an air-tight vessel at room temperature for 48-72 h.

Modification (hydrothermal treatment)

Hydrothermal treatment of dry wood was carried out in a pilot scale batch autoclave in a steam medium and under pressure slowly raising the temperature up to 180°C and holding for 2 hours under these conditions.

Pelletization

Flat die type pelletizator (*Amandus Kahl GmbH*) was employed for pelletization of dry and milled MW with the fractional composition ≤ 2 mm. Material was pressed through a flat die with holes of diameter 6 mm by pan grinder rollers, formed into endless strands, and then cut to the desired particle length by means of knives. The temperature on the die was about 100-110°C.

Carbonization and activation

In the next step, pelletized MW was carbonized in an electric furnace heated to the 600°C at a rate of 2.0°C/min. The granules (1-3 mm) of the carbonized MW were inserted in a stationary kiln with a steam-superheating device and activated at the temperature 850°C for 90 min at the steam – charcoal ratio 3 : 1.

RESULTS AND DISCUSSION

Pelletization of modified GA wood

High-quality pellets from modified GA wood can be made with initial moisture contents of 6-10% w. b., and water contents above or below this range would lead to lower quality pellets (Table 1).

Table 1: Impact of the moisture content of raw MW before pelletization on the properties of pellets

Moisture content [%]	4	6	8	10	12
Yield [%]	88.1	92.9	92.3	92.2	88.4
Bulk density [g/l]	753	760	742	740	726
Apparent density [g/cm ³]	1.329	1.355	1.345	1.362	1.375
Hardness [kgf]	52±8	58±8	57±4	54±8	46±6

Carbonization and activation of modified GA wood pellets

The obtained MW pellets were carbonized for further activation. Dense and high-quality carbonized MW pellets can be made with initial moisture contents of 6-10% w.b. before pelletization, and water contents above or below this range would lead to lower quality carbonized pellets (Table 2).

Table 2: Impact of the moisture content of raw MW before pelletization on the properties of carbonized pellets and GAC

Moisture content [%]	4	6	8	10	12
Carbonization (600°C, 2°C/min)					
Ash content [%]	3.02	2.15	2.65	2.35	2.2
Bulk density [g/l]	570	605	596	602	597
Apparent density [g/cm ³]	1.161	1.160	1.157	1.144	1.107
Hardness [kgf]	18± 4	22± 4	23± 3	20± 3	16± 4
Activation (850°C, 90 min, steam and charcoal ratio 3:1)					
Ash content [%]	6.29	4.43	5.31	4.45	4.35
Bulk density [g/l]	399	436	438	457	439
Yield [% o. d. MW]	18.1	20.3	20.2	20.9	20.8
Attrition [%]	6.8	5.3	6.0	4.3	4.9

The best AC yield is obtained from the MW prepared from pellets with the initial moisture content from 6 to 12%. Only a moisture content of 4% shows decreased properties (Table 2). Therefore, if microporous sorbents with a narrow distribution of

pores' dimensions are necessary, the pelletization with the moisture content in a range of 6-12% is preferable. Because the yield of this AC is 20-21% (o.d. MW), the ash content is comparatively low, i.e. 4.3-5.3%, which meets the requirements of most standards for the gas cleaning GAC (Table 2). The carbonized granulated material retains its physical and mechanical properties after superheated steam activation at 850°C. Comparative activation results of the carbonized MW pellets and coconut shell charcoal, activated at 850°C for 90 min and the steam-charcoal ratio 3:1, can be seen in Table 3.

Table 3: Properties of GAC obtained from MW pellets and coconut shells

Quality indicators	MW pellets	Coconut shells
BET surface [m ² /g]	1338	1390
Total pore volume [mm ³ /g]	880	686
Micropore volume [mm ³ /g]	398	500
Attrition [%]	4.3	4.8
Bulk density [g/l]	457	488

Dense and mechanically strong microporous GAC with a narrow distribution of pores' dimensions was prepared by superheated steam treatment. The porous structure characteristics were close to those of the coconut shell AC: BET surface 1338 and 1390 m²/g, total pore volume 880 and 686 mm³/g, and micropore volume 398 and 500 mg/g, respectively. So, these carbon materials would be promising products from renewable biomass.

CONCLUSIONS

The best results obtained, if the treatment time at 180°C is 2 hours and the relative moisture content is 8%. The porous structure characteristics were close to those of the coconut shell AC. By environmentally friendly modification of soft structure deciduous wood that is out of high grade demand, it is possible to produce an effective sorbent for industry - for purification of gaseous emissions.

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**Session Five:
Poster Session 2**

Modification of Domestic Timbers by Impregnation Using Supercritical Carbon Dioxide - A Look on the Process

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Keywords: Impregnation, supercritical carbon dioxide, wood modification

ABSTRACT

Wood samples were treated with different kind of chemicals. During this process, the compounds may deposit in the lumens and the cell walls causing a change of wood properties. In many important domestic wood species, particularly in spruce wood, conventional impregnation procedures using water or organic solvents achieve only superficial penetration with depths of only a few millimetres. Thus a solvent is needed, which enables the complete penetration of the wood without damaging its structure. It was previously shown that supercritical impregnation resulted in reduced water uptake and complete penetration of the specimens. Thus, the objective of the studies described here is to verify the suitability of supercritical carbon dioxide (scCO₂) as solvent for the impregnation process. In comparison to the classical vacuum-pressure impregnation the supercritical infiltration shows the similar load (weight percentage gain), but in shorter time and with less amount of chemicals used in the treatment process. Another advantage of supercritical impregnation is that no additional drying after the process is needed.

INTRODUCTION

Native lumbers are often not suited for construction trade or façade applications because of low dimensional stability, low durability or low mechanical strength and are excluded from the market by tropical lumbers or other materials (such as plastics or metals). One possibility to accomplish this aim is the impregnation of wood with silicon containing substances such as silane based nanosols or silicones (Mai and Militz 2004a, b). Most of these compounds are difficult to solve in water and must be applied in organic solvents or emulsified in water. Impregnation using supercritical carbon dioxide is therefore an alternative, particularly for refractory species such as spruce (Danzig *et al.* 2006, Danzig *et al.* 2007). Carbon dioxide becomes a supercritical fluid at a temperature above 32°C and a pressure exceeding 7.2 MPa (72 bar, 1044 psi), a physical state which has the properties of either gas or liquid. Under pressures from 10.0 to 40.0 MPa and at temperatures of 35 to 70°C supercritical carbon dioxide can be used as a solvent for non-polar substances, and is applied in established processes like the recovery of natural flavours or the decaffeination of coffee and tea. The process temperature for wood impregnation does not need to be higher than 40°C, depending on the chemical. Because of its low surface tension, supercritical CO₂ intrudes deeply into the wood without swelling it.

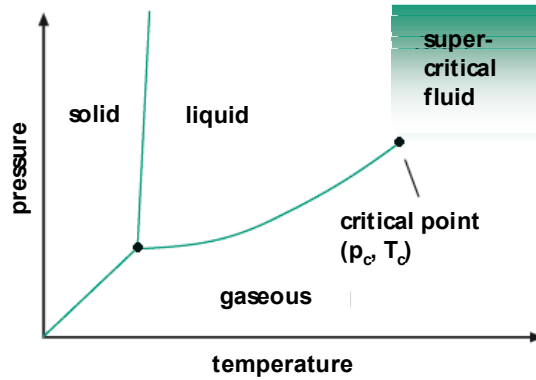


Figure 1: Phase behaviour of carbon dioxide

Any mechanical damage is minimised if care is taken during the pressure built-up and pressure release during the impregnation (Jelen *et al.* 2003). Another advantage of supercritical carbon dioxide is that supercritical carbon dioxide becomes a gas after pressure release and there is no solvent left in the wood (Jelen *et al.* 2006, Jelen *et al.* 2007).

EXPERIMENTAL

For impregnation with supercritical carbon dioxide at Fraunhofer UMSICHT the pilot plant station depicted in Figure 2 was used.

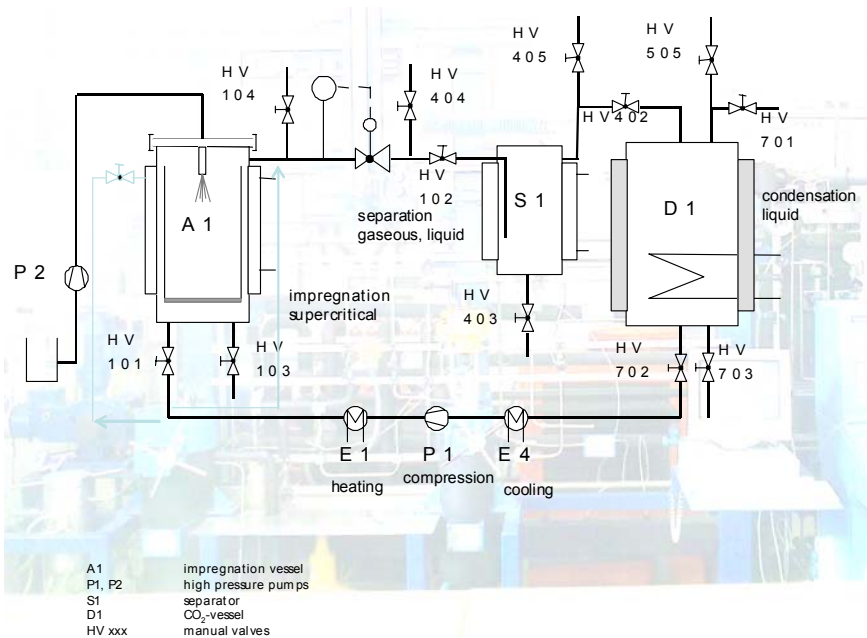


Figure 2: Pilot plant station for the impregnation used at Fraunhofer UMSICHT

First the carbon dioxide from the storage tank (D1) was cooled to get liquefied and pumpable. After that the carbon dioxide was heated to up to 40°C and pressurized up to 15 or 20 MPa. Afterwards it flows through a pre-vessel or directly with the impregnation agent into vessel A1. When impregnation time was over the pilot plant

station was depressurized and the impregnation agent precipitated on and in the wood. In every experiment the samples were arranged in the same way (Figure 3). This makes the interpretation of intrusion easier and the results more comparable.



Figure 3: Wood samples after scCO₂ impregnation

The impregnation process described above and depicted in Figure 2 is not suitable for all impregnation agents. Depending on the physical-chemical properties of the substance or the formulation of different chemicals the impregnation process has to be adapted. To solve this problem, variations of impregnation processes were tested. First trial was to spray the chemical overhead into the vessel with parallel flow to the carbon dioxide. The second trial was to put the wooden specimen between two sieves and overlaying the chemical. Depending on the wood kind and the properties of the chemical the process may be a static or dynamic process or a mixture of both. For each process the best parameters of pressure and temperature have to be investigated.

RESULTS AND DISCUSSION

In the beginning the amount of uptake in comparison to the vacuum-pressure method was less. But during investigation the amount was similar or sometimes higher and the intrusion of supercritical carbon dioxide is very good with shorter time of impregnation. It was found out that for a pair of wood kind and chemical the process parameters have to be tested very carefully to get good results.

CONCLUSIONS

On the one hand it was shown, that impregnation of wood with supercritical carbon dioxide is viable, but the impregnation process has to be revised. On the other hand, the results show that supercritical carbon dioxide completely penetrates through the wood. In comparison to the vacuum-pressure method, the amount of uptake was low in the beginning of investigation. But the intrusion of supercritical carbon dioxide is very efficient with shorter time of impregnation (Deerberg, Danzig and Jelen 2006). Further investigations are still running.

ACKNOWLEDGEMENTS

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Dimensional Stabilization by Injection of Urea Compound and Glycol Compound under Pressure. Drying Tests of Injected Japanese Cedar Boxed-Heart Timber

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Keywords: Dimensional stabilization, urea compound, glycol compound, anti-shrink efficiency, Japanese cedar.

ABSTRACT

Injection of urea compound and glycol compound under pressure (DS treatment) is an easy treatment of the dimensional stabilization for green wood. To clear the effects of DS treatment, we examined the deformation of injected Japanese cedar boxed-heart timber during drying. As a result, the anti-shrink efficiency: ASE of the DS injected specimens was about 33 % in the T direction under both air-dried and oven-dried conditions. This effect reduced the occurrence of cracks, and the shrinkages in the T and R directions were nearly equal because the DS specimens had dried to keep those certain square shapes. Then, we applied colour reaction chemical to the cross sections of the air-dried specimens, and calculated the area of the part saturated with DS chemical. As a result, at the range from the end to 50 mm inside those were completely saturated, and at the other range those were partially saturated from the surface to 15 mm inside. There was a high correlation between the saturation and the anti-shrink effects. By the above explains, we cleared the dimensional stabilization effect of DS treatment to practical size timber.

INTRODUCTION

To use timber, it is very important to control and stabilize dimensional change of the green timber in drying process, because it prevents the occurrence of cracks and maintains its original square shape, thus it can improve its nature of design and preservation etc. Therefore various timber-modification methods have been developed recently. PEG (Polyethylene glycol) treatment and WPC (Wood plastic combination) treatment are the examples. Those methods control the shrinkage of timber by the bulking effect, and it is said that those ASE (Anti-shrink efficiency) are over 80 % in the appropriate condition. So those methods can achieve almost perfect dimensional stabilization, but there are some practical issues that an enough drying is necessary before the method and its many treatment processes increase the total cost. After all, we focused on the method of injecting urea compound and glycol compound under pressure, which an enough drying isn't necessary before and whose cost is lower than that of other methods. The purpose of this study is to verify the actual dimensional stabilization effect of this treatment by drying tests of injected Japanese cedar boxed-heart timber.

EXPERIMENTAL

Specimens

We prepared Japanese cedar (*Cryptomeria japonica* D.Don) boxed-heart timber yielded in Miyazaki prefecture as sample timber. Those initial moisture contents in green condition were between 50% and 80%. Among the prepared specimens, some of them were treated by the following process. The prepared chemical was DS chemical (Product name: Koshi-plus DS, made in Koshii Preserving Co. Ltd.). DS chemical is a solution of mainly 5% urea compound and 2% glycol compound like cosmetics. The injecting process followed JIS (Japanese Industrial Standard), concretely it was a Bethel method and the injecting time was 2 hours, the pressure was 1.5 Mpa. The data of the prepared specimens are shown at Table 1.

Table 1: Data of specimens

Sample name	Size [mm]	Number	Measurement points	DS content [kg/m ³]
DS-a	105×105×1000	2	6 (T)	263.6
Cont-a		2		0
DS-b	105×105×50	15	2 (T), 2 (R), 4 (L)	273.0
Cont-b		15		0
KD-b		15		0
DS-c	105×180×3850	2	6 (T)	175.1
Cont-c		1		0

DS: Specimen saturated with DS chemical, Cont: Control specimen saturated with water, KD: Specimen kiln-dried once before the test.

Drying Tests

Three types of tests performed on each specimen are as follows.

(-a) specimens: Dried in the temperature-controlled room at 25°C, 65%RH.

(-b) specimens: Dried in the thermostatic chamber at 60 °C, free moisture adjustment for 8 days, afterward at 105 °C, free moisture adjustment for 2 days to dry completely.

(-c) specimens: Dried in the residence room as beams.

Each specimen was measured the weight and dimensions at each period of time, then we calculated the moisture content and shrinkages. We used a digital calliper whose measurement unit is 0.01 mm.

Colour Reaction Tests

After the drying tests, we applied colour reaction chemical to the cross sections of the air-dried (-a) specimens and (-c) specimens, and calculated the area of the part saturated with DS chemical. Urea compound of DS chemical makes condensational reaction (Ehrlich Reaction) with DAB (p-Dimethylaminobenzaldehyde: $(\text{CH}_3)_2\text{N}-\text{C}_6\text{H}_4-\text{CH}=\text{O}$) under acidic condition. This reaction makes yellow pigment, thus we can calculate urea saturated areas of the specimens by image analysis. In this test, we firstly took pictures of each cross section of the specimen. Then we painted hydrochloric acid (2N) by brush to make it under acidic condition, shortly after we painted DAB as well. After the pigment settled, we took pictures as well as first photographing. At last we picked out the cross section pictures and the coloured part pictures from before and after pictures, then calculated the saturated area ratio, and verified the correlation between the saturation and the shrinkage.

RESULTS AND DISCUSSION

Figure 1 shows changes of (-a) specimens and (-c) specimens in shrinkage and moisture content. In both tests, there were definite differences in the shrink process between DS and Cont.

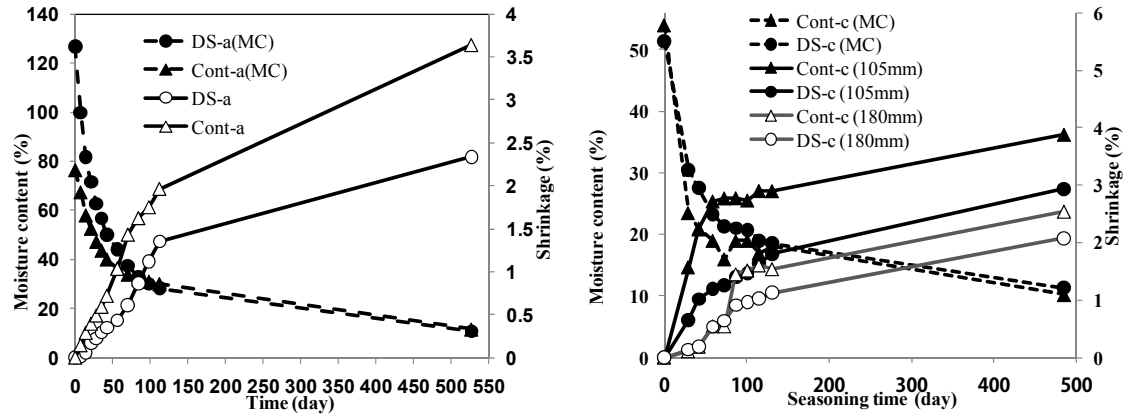


Figure 1: Changes in shrinkage and moisture content of specimens during drying.

Figure 2 shows changes of (-b) specimens in shrinkage. The shrinkages in the T and R directions were nearly equal because the DS specimens had dried to keep those certain square shapes. On the other, Cont specimens had dried with cracking occurs and more shrinking than DS specimens.

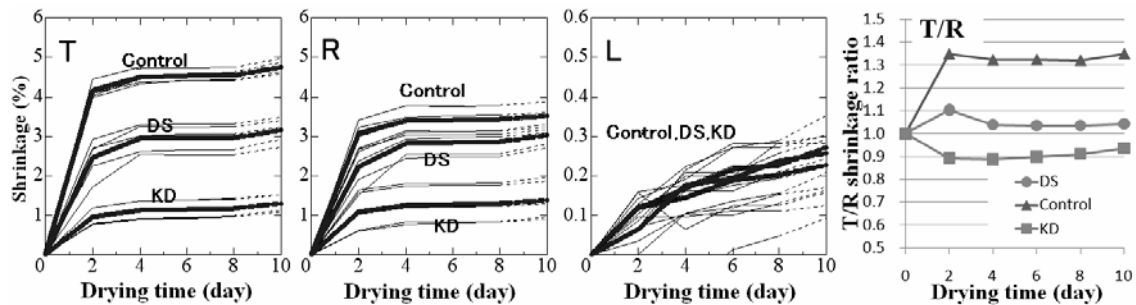


Figure 2: Changes in shrinkage of T, R, L directions and T/R ratio of (-b) specimens.

Table 2 shows numerical values of shrinkage and ASE of specimens. ASE was calculated by the below (Eqn. 1).

Table 2: Shrinkage and ASE of specimens

Sample name	Shrinkage [%]	ASE [%]
DS-a	2.34	35.7
Cont-a	3.64	
DS-b (T)	3.16	33.6
Cont-b (T)	4.76	
DS-b (R)	3.03	14.0
Cont-b (R)	3.53	
DS-c (180 mm)	2.93	24.2
Cont-c (180 mm)	3.87	
DS-c (105 mm)	2.07	18.4
Cont-c (105 mm)	2.54	

$$ASE (\%) = (1 - (DS \text{ shrinkage}) / (\text{Cont shrinkage})) \times 100 \quad (1)$$

Figure 3 shows DS saturated cross sections of DS-a, and correlation between DS saturation and shrinkage of (-a) specimens. After drying test, (-a) specimens were divided into 20 small specimens. At the range from the end to 50 mm inside, those specimens were completely saturated with DS chemical, and at the other range those were partially saturated from the surface to 15 mm inside. Also there was a high correlation between the saturation and the anti-shrink effects.

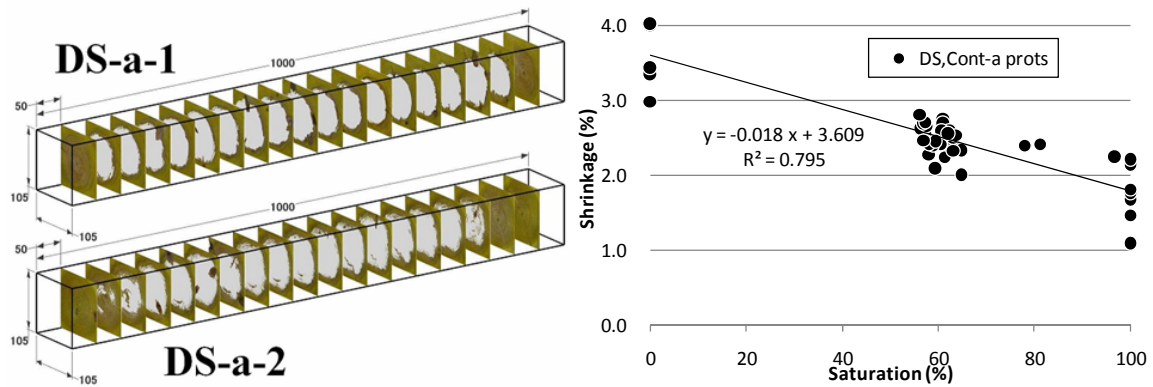


Figure 3: DS saturated cross sections and correlation between saturation and shrinkage of specimens

CONCLUSIONS

The effect of dimensional stabilization of DS treatment for Japanese cedar was verified by ASE, and the result was about 33 % in the T direction. This means that DS treatment can reduce 1 / 3 amount of shrinkage, thus it can reduce the occurrence of cracks mostly. This amount of ASE is less than that in PEG treatment and WPC treatment, but DS treatment is easier in treatment process and smaller in cost, so it can be said that the effect is reasonable in process and cost. DS specimens had dried to keep those certain square shapes, thus the amounts of shrinkages in the T and R directions were nearly equal. There was a high correlation between the amount of urea saturation and that of shrinkage in DS treated Japanese cedar. By the above explains, we cleared the dimensional stabilization effect of DS treatment to practical size timber.

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Impregnation and in-situ Polymerization of Isobornyl Acrylate in Wood for Stabilization and Densification

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Keywords: Beech wood, durability, impregnation, polyacrylate, stabilization

ABSTRACT

The preservation products that have been used so far to treat the wood intended for uses in hazard class 4 implied treatments with broadly active toxic biocides like creosote or multi-salts formulations which are incompatible with the new implementation of the European Biocide Directory. In this context, the objective of this work is to study an alternative way to improve the performance of wood against biological degradation. A possible answer involves the formation of wood polymer composites (WPC) obtained by impregnation of monomers into the wood followed by *in-situ* polymerisation. Not only do the examined treatments aim at conferring a dimensional stability but also at improving the mechanical properties through wood densification. Isobornyl acrylate monomer has been chosen for its hydrophobic properties and furnished by ARKEMA in order to evaluate its performance in WPC applications. The influence of impregnation conditions such as monomer dilution in different solvents at different concentrations on composites final properties has been studied. Each treatment has been characterized by the weight percentage gain (WPG) of wood samples. Chemical analyses by FT-IR and GPC have allowed confirming the presence of polyacrylate into the wood structure. The impregnation solvent and dilution ratio has been pointed out to impact resistance of polymerized product on water leaching and antishwelling efficiency. These results have been analyzed regarding interactions between cell walls and isobornyl polyacrylate using ESEM. A strong increase in Brinell hardness has been obtained for modified wood. Finally, microbiological tests have been performed to evaluate the resistance of the composites against different decay fungi.

INTRODUCTION

Wood, despite its mechanical properties and its ecological characteristics, has drawbacks such as dimensional instability and susceptibility to biological degradation. Different modifications of wood have been investigated so far to improve wood's properties. Thermal modification improved decay durability and wood dimensional stability, chemical modification with anhydrides (Rowell 2005), furfuryl alcohol (Lande *et al.* 2004), and lumen modifications with acrylic polymers (Ellis and O'Dell 1999) are well known potential ways of enhancing physical properties. The disadvantages of

chemicals can be their high toxicity and their petroleum based source. The interest of acrylic polymers is enhanced as they could now be obtained by using green chemistry, from bio-based by-product, glycerol (Deleplanque *et al.* 2010). The main objective of our project consists in examining the potential of different acrylic monomers. We aim to study the influence of chemical structure of such monomers on the process (impregnation rate, wood percentage gain) and on the composite properties (antiswelling efficiency, lixiviation, biological and mechanical resistance). In this work, we propose to investigate a new candidate chosen for its hydrophobic character, isobornyl acrylate.

EXPERIMENTAL

Treatment

Beech wood blocks (5x10x30mm³) were preliminary dried at 103°C until constant weight. They were then immersed in pure, diluted, or emulsified isobornyl acrylate monomer with 2% benzoyl peroxide as initiator, in impregnation reactor as shown in figure 1. The impregnation period is 0.8 bar vacuum for 30 minutes followed by 3 bars pressurized air for 30 minutes. Impregnated samples were then heated 2 hours in 80°C ventilated oven to induce polymerization in-situ, and dried at 103°C until stabilization. Weight percent gain (%) was calculated as the ratio of sample mass uptake (ΔM) on initial dried mass (M_0), following eqn 1.

$$\text{WPG (\%)} = (\Delta M / M_0) \times 100 \quad (1)$$

Chemical analysis of wood composites

FTIR spectra wood polymer composite were recorded as KBr disks on a Shimadzu FTIR 8400 spectrometer. Finely divided sawdust (1% in weight) was dispersed in a spectral grade KBr matrix and pressed to form 200mg pellets. Weight molar mass distribution of polymers extracted by chloroform from grounded samples was determined with respect to polyethylene glycol standards by GPC equipped with a linear Waters Phenogel HR1 column. All samples were diluted in DMF at weight ratio of 2.0%. DMF eluent was delivered at a flow rate of 1.0 mL.mn⁻¹ at 35°C.

Properties of wood composites

Treated and untreated wood blocks were soaked in water until constant mass then dried at 103°C for 24h. Volumetric swelling (S) was determined following Eqn2, where V_w and V_d stands respectively for wet and dried volume. ASE was calculated following Eqn 3, where S_0 and S_1 stands respectively for swelling of untreated and treated specimens:

$$S (\%) = 100 \times (V_w - V_d) / V_d \quad (2)$$

$$\text{ASE (\%)} = 100 \times (S_0 - S_1) / S_0 \quad (3)$$

Water leaching was performed according to a method adapted from NF X 41-575 French standard. Treated or untreated wood specimens were placed in a flask filled with 450mL agitated 20°C distilled water. After leaching, samples were dried at 103°C and weighed in order to determine the loss of weight. Brinell hardness was determined

following EN 1534 European standard. A 10 mm diameter steel ball was pressed into tangential section of solid wood treated and control specimens. A treated sample was cut by microtome and surface analysed with Environmental Scanning Electron Microscope (ESEM) Quanta 200 Phillips device.

Decay resistance

Chemically treated and untreated wood specimens were prepared according to EN 113. After weathering, samples were exposed to brown rot basidiomycetes, *Poria placenta*, for 12 weeks at 22°C and 70% RH in a climate chamber. Treatment was evaluated by weight loss determination after time exposure.

RESULTS AND DISCUSSION

In first experiments, wood blocks were impregnated with pure isobornyl acrylate monomer with initiator. FT-IR spectra confirm the *in-situ* polymerization of isobornyl acrylate by the presence of a non conjugated carbonyl band at 1730 cm⁻¹. Analysis of molecular weights of chloroform extracted polymers was about 12500Da according to GPC analysis. In order to improve the impregnation of the acrylic monomer within the cell walls, we investigate the effect of several solvents of different polarities and swelling capacities. Results are gathered in table 1. High WPG shows an efficient impregnation and fixation, due to efficient swelling of the wood structure and efficient polymerization of the monomer. The small decrease of WPG after leaching indicated a good polymerization and retention of the acrylic monomer, when impregnated in acetone, while use of DMF seems to decrease the polymerization degree leading to small leachable oligomers or unpolymerized monomer.

Table 1: Impregnation results for different solvents

Sample	solvent	WPG [%]	WPG after leaching [%]
A	acetone	54	46
B	DMF	28	9
C	hexane	41	32
D	water ^a	33	nd

^a emulsion

The results show clearly that dilution of monomer with acetone gives the best results, meaning that polymerization occurs more efficiently than with other solvents tested. We further examined leaching and ASE performances using acetone at different concentrations, as shown in table 2.

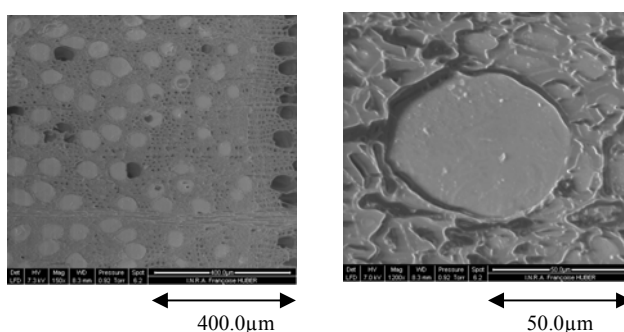
Table 2: Influence of dilution on composite properties

Sample	% product	WPG [%]	WPG after leaching [%]	ASE [%]
E	100	57	54	<1
F	75	74	68	<10
A	50	54	46	20
G	25	24	17.5	28

Sample E stands for the non diluted product as reference. It can be pointed out that low ASE values are obtained traducing poor efficiency of this treatment suggesting that it hardly penetrates and swells the cell walls. The more concentrated the monomer is, the

less the leaching rate and ASE value: that brings us to light that firstly biggest polymers would stay in the lumen, and remain unleached. Secondly low polymerized products would swell the cell walls better, but are too leached.

In order to control the presence of product in lumens, an ESEM image was recorded with E sample: it underlines that lumens are almost filled with polyacrylate (1a) but without attachment or penetration in cell walls (1b): this shrinking effect in lumens has already been observed with methyl methacrylate impregnation (Rowell, 2005).



Figures 1a (left) and 1b (right) : ESEM micrograph of wood-isobornyl polyacrylate composite

The filling of the lumens is known to enhance mechanical properties of wood. It was checked with Brinell hardness determinations: initial hardness of beech wood ($4\text{N}\cdot\text{mm}^{-2}$) was 4 fold increased ($12\text{N}\cdot\text{mm}^{-2}$) for E sample and only doubled for G sample, showing incomplete filling when the monomer is directed in wood cells by acetone. According to preliminary biological results, decay resistance against *Poria placenta* was not improved with regard to untreated wood. This behaviour is in coherence with low ASE and the absence of interactions of polymer with cell walls.

CONCLUSIONS

These first results concerning impregnation and polymerization in-situ of acrylate monomers are coherent: isobornyl polyacrylate is not efficient for wood stabilization. However it leads to a gain in hardness. New polyacrylate candidates having potentially more affinity to wood are under study in the laboratory.

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Effect of Artificially Accelerated Weathering on Wettability and Surface Chemistry of Wax Treated Wood

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Keywords: contact angle, CIEL^{*}a^{*}b^{*}, FTIR, wax emulsion, water repellent, weathering

ABSTRACT

Waxes are used for treatment of wood for centuries. Three types of wax emulsions of two different concentrations were used for vacuum impregnation of Norway spruce wood specimens, namely; emulsion of montan wax (LGE), an emulsion of polyethylene (WE1) and an emulsion of oxidized polyethylene (WE6) wax. Samples were exposed to artificially accelerated weathering (AAW) for 500 cycles. Before and after AAW colour, contact angle and moisture content were determined. Chemical changes of exposed surfaces were also investigated with ATR-FTIR spectroscopy. Moisture content measurement showed that the best hydrophobic effect was determined at LGE treated wood. Furthermore, FTIR analysis of artificially weathered wood surfaces showed that LGE wax emulsion slowed down the colour changes and chemical degradation of wood.

INTRODUCTION

Wood is one of the most important materials in construction applications. When wood is used outdoors a variety of different combination of environmental factors degrades the main wood constituents. These processes are described as weathering (Temiz *et al.* 2007). Photochemical degradation is manifested by an initial colour change followed by loss of gloss, roughening and checking. UV light acts in combination with moisture, temperature, environmental pollutants and oxidative agents to depolymerise lignin and cellulose (Chang *et al.* 1982, Evans *et al.* 2008). Changes in wood colour are thus direct indication of chemical or biological changes. Increased environmental pressures in the last few years resulted in a development of non-biocidal solutions for wood protection, such as water repellents. The most important water repellents used are waxes, particularly paraffin waxes. However, waxes are nowadays more and more used to prolong life expectancy of wood. There are several commercial applications based on the wax treatments on the market (Berninghausen *et al.* 2005). As, this wood is designed for outdoor use, it is of significant importance to understand processes during weathering. The objective of this study was to evaluate contact angle, colour and chemical changes of wood impregnated with various waxes during artificially accelerated weathering (AAW).

EXPERIMENTAL

For impregnation, three types of wax emulsions, of two concentrations, were used. Namely; an emulsion of montan wax (LGE), an emulsion of polyethylene (WE1) and an emulsion of oxidized polyethylene (WE6) wax. Norway spruce (*Picea abies*) wood samples (20T mm × 100R mm × 150A mm) were treated with various wax emulsions

prior AAW (vac. – 30 min; pres. – 180 min; vac. – 10 min), as can be seen from table 1. The uptakes of emulsions in specimens were determined gravimetrically. After three weeks of conditioning the impregnated and control samples were exposed to AAW for 500 cycles. Cycles comprised of artificial rain, UV and IR radiation. One cycle lasted 60 min. Before and after AAW the colour (CIEL*a*b*) and contact angle (sessile drop method) of control and treated samples were determined. After every 100 cycles MC of all samples was gravimetrically determined and FTIR spectra recorded. Six samples were used for each treatment; five specimens were exposed to AAW, one sample of each treatment/control was placed in dark and dry place for 6 weeks in parallel.

RESULTS AND DISCUSSION

Wax emulsions used in this experiment had different dry contents. They varied between 4.9% (LGE-A) and 17.8% (WE6-B) (Table 1). It is clearly evident that retention was influenced by dry content of wax. The main reason for lower penetration of emulsions with higher dry content is the fact that particles in emulsion are too big (100 μm) to penetrate in the cell wall, and even more, they form barrier on the surface of cell wall and reduce penetration of the water to the cell wall as well (Lesar and Humar 2010). Contact angles were measured before and after AAW. The result is rather surprising, as impregnation of wood with waxes did not result in higher but in lower contact angles than observed at control samples. There are several reasons for this phenomenon: presence of hydrophilic emulsifiers and inadequate film formed on the surface of wood treated with WE6 emulsion.

Table 1: Retention of emulsions and influence of AAW on wood contact angles. In parallel contact angles of wood stored in dark are given. Standard deviations are given in the parenthesis.

Wax emulsion	Wax content (%)	Retention (kg/m ³)	Contact angle (°)		Contact angle (°)	
			before AAW	after AAW	before storage	after storage
LGE-A	4.9	261 (47)	33 (8)	88 (12)	33 (9)	35 (9)
LGE-B	11.7	259 (35)	19 (6)	81 (15)	20 (4)	21 (5)
WE1-A	8.2	243 (19)	96 (5)	59 (12)	107 (3)	97 (8)
WE1-B	16.5	151 (20)	94 (9)	57 (14)	93 (11)	66 (12)
WE6-A	8.3	229 (41)	4 (1)	54 (14)	4 (1)	7 (1)
WE6-B	17.8	189 (5)	8 (3)	54 (15)	7 (1)	7 (1)
control	0	0	126(5)	85 (25)	122 (6)	115 (5)

There are small crystals formed on the surface of the wood impregnated with WE1 and WE6 that prevents formation of clearly shaped droplets on the surface. The weathering resulted in changes of contact angles of the control and wax treated wood. However, it should be considered, that contact angles at impregnated and control wood specimens did not change significantly during storage (Table 1). This indicates that changes of the contact angles are predominately caused by weathering and are not result of the naturally occurring processes. Moisture content (MC) of treated and control samples during the AAW was more or less constant during all weathering cycles with exception of the first one (Table 2). MC of weathered control specimens was higher for approximately 25% than the MC of wax treated wood. However, there was no correlation between contacts angles determined on the surface of the wax treated wood and moisture content during AAW. It is believed, that the reasons for lower MC of impregnated specimens can be summarized in two main reasons. Firstly the cell lumina

in outer part of the samples were at least partly filled with waxes and this physically prevents moisturizing. Secondly there were thin film-barriers formed on the surface of the wooden specimens, which slow down water movement (Lesar and Humar 2010). Colour of the wood exposed to the AAW changed considerably. Colour changes, after 500 cycles of AAW, of wax treated wood was less prominent than the colour changes of control ones. The most prominent colour changes appeared after first 120 cycles of AAW, afterwards colour did not change that obviously. The same samples (LGE-B) where the lowest colour changes were determined, the lowest MC during AAW was measured as well (Table 2). There is rather good correlation between MC and colour changes observed ($r^2 = 0,84$). Specimens that were less moist during AAW were less discoloured as well.

Table 2: Moisture content and colour changes of control and wax treated samples during AAW.

Wax emulsion	Moisture content (%)			Colour change			
	0 cycle	120 cycles	500 cycles	ΔL^*	Δa^*	Δb^*	ΔE^*
LGE-A	3.3 (0.2)	32.9 (3.4)	33.6 (2.8)	-18.3	2.3	-4.2	18.9
LGE-B	3.2 (0.2)	29.3 (3.7)	31.0 (2.1)	-15.7	1.6	-4.6	16.5
WE1-A	3.1 (0.4)	38.0 (7.2)	32.3 (4.9)	-17.4	1.2	-5.2	18.2
WE1-B	3.0 (0.1)	33.4 (2.4)	33.9 (3.8)	-16.6	1.3	-5.2	17.5
WE6-A	3.2 (0.4)	35.6 (2.4)	31.5 (2.9)	-17.6	1.1	-4.1	18.1
WE6-B	2.7 (0.2)	34.0 (3.6)	34.1 (3.2)	-18.1	2.5	-2.9	18.5
control	4.1 (0.2)	45.8 (4.8)	43.9 (2.4)	-21.4	1.5	-2.5	21.6

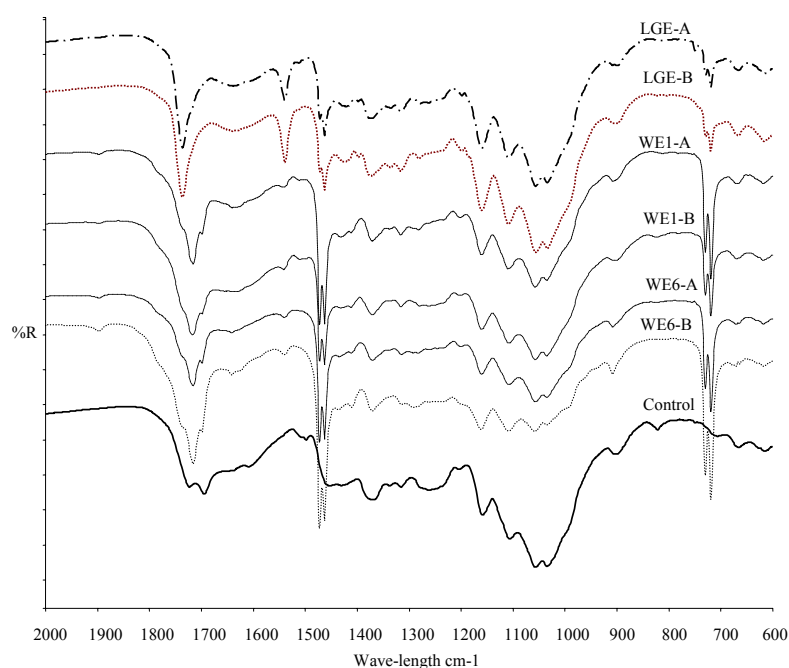


Figure 2: FTIR spectra of un-impregnated and wax treated samples after 500 cycles of AAW.

In order to elucidate chemical changes of wood surfaces FTIR analysis was applied. The most characteristic bands for FTIR spectra of WE1, WE6 and LGE waxes are $1725\text{ cm}^{-1} - 1700\text{ cm}^{-1}$, $1485\text{ cm}^{-1} - 1445\text{ cm}^{-1}$ and $730\text{ cm}^{-1} - 710\text{ cm}^{-1}$. FTIR spectra of impregnated wood samples reflect wax treatment, after AAW also. Photo-induced degradation of untreated and treated wood lead mainly to changes in the absorption intensity at $1740\text{ cm}^{-1} - 1720\text{ cm}^{-1}$, 1600 cm^{-1} , 1510 cm^{-1} and 1261 cm^{-1} (Fig.1). However, the same pattern of degradation is reported in literature as well (Temiz *et al.*

2007, Evans *et al.* 2008). The intensity and changes of these bands are related to changes in chemical composition of the functional groups and chemical structure of wood components. The most significant change as a result of AAW appeared at peak 1510 cm^{-1} which is a characteristic peak for lignin C=C stretching vibrations of the aromatic rings present. This peak almost disappears within few hours of AAW (Colom *et al.* 2003). Degradation of lignin was slightly reduced due to the impregnation with WE1-A, WE1-B, WE6-A and WE6-B. However, the least prominent changes of FTIR spectra were determined at LGE-A and LGE-B impregnated wood what is in line with colour and moisture measurements as well. From the practical aspects, it is very important, that the bands related to waxes remained even after weathering.

CONCLUSIONS

Impregnation of wood with waxes influences the wood performance during AAW. Contact angles data are not in line with moisture content observation during AAW. MC of all wax treated samples was considerably lower than MC of control samples. Results of colour and chemical changes indicate that LGE-A and LGE-B wax to certain extent limit photo-degradation of wood.

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Weathering Results of Wax Modified Wood after Two Years Outside Exposure

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Keywords: Outdoor exposure, wax impregnated wood, weathering

ABSTRACT

This paper presents the results of wax impregnated wood weathered for two years under outdoors conditions. Wax impregnated beech does not show a reduced frequency of cracks compared to native controls. However the cracks observed are smaller and mainly situated on the surface compared to untreated wood. The influence of water penetration as well as blue stain infestation remains limited on the surface. The dimension stability is improved Greying took place due to the absence of pigments or coatings. However, the results indicate a long-time use of such products due to the prolongation of wood decay. The use of UV protection and fungicides is necessary.

INTRODUCTION

Wood is a susceptible material to many abiotic factors such as solar radiation, wind abrasion and water uptake (Feist and Hon 1984). The water uptake causes wood swelling and therefore formation of cracks and leaching of degraded phenolic compounds created from lignin. Furthermore, the infestation by fungi becomes possible. Low temperatures lead to a congealing of water which causes a volume extension of about 9% (Riedel *et al.* 1999) and wood degradation. There are many methods to retard or decrease wood decay by weathering. A conventional possibility is the use of paints or stains. But also the application of chromic acid or chemical stabilizers is described in literature (Williams 2005). Other methods are wood modification and the treatment of wood with water repellents. A temporary improved color stability is reported for acetylated wood (Imamura 1993, Hon 1995). Water repellents are known to decrease the water uptake and crack formation. In early stage of weathering, they may decrease the amount of leached degradation products (Minemura *et al.* 1983, Feist 1987) or secondary extractives on the surface. But it is concluded, that the modification of the cell wall or the filling of lumen has only a moderate effect on the UV stability (Williams 2005). Waxes are assigned to the water repellents. Tests from window frames treated with paraffins showed a low crack frequency and no fungi decay after 20 years (Feist and Mraz 1978a). Wood treated with a resin/wax-mixture and additional UV stabilizers or fungicides did show a decreased greying and minor crack formation (Mundigler and Rettenbacher 2005). This article presents the test results of two different hot melting wax types after two years of weathering under consideration of crack formation, coloring and water uptake.

EXPERIMENTAL

Materials and general information

Specimens of European beech for the outdoor exposure were manufactured according to EN 927-3 (2000). Impregnation of the wood was carried out with an amid wax 1 (Licolub FA5; Clariant Company) and a paraffin wax 2 (Paraflint C80; Sasol company) (0.1-12 bar at 100°C). The specimens were weathered on the test field (Wood Biology and Wood Products Goettingen), with Southern exposition (45°). The climate data from the weather station Goettingen were used.

Evaluation

The weight determination was carried out one time per month. The evaluation of cracks (frequency, intensity) followed the standard EN ISO 4628-4 (1997). Additionally, the depth of cracks was measured (rank 0-4; 0: no cracks; 4: cracks from one surface to the other). These parameters were determined every three months. Furthermore, the specimens were scanned in the same frequency (EPSON Expression 10000 XL; Laser Soft Imaging). The images were evaluated by applying ADOBE Photoshop 8.0 according to the CIE-Lab-Modus (system of additive coloring). The following parameters were calculated and used: lightness (*L*) and chroma (*C*). Every second specimen was cut in three pieces (approx. 100 mm) after the test period of two years. Thus, data about the inner wood parts were obtained.

RESULTS AND DISCUSSION

Water uptake

The water uptake is demonstrated in Figure 1. Native beech showed a change of mass due to the water uptake between -4 and 46%. The water uptake of wax impregnated beech did never exceed 7% due to the filling of wood lumina with wax deposits.

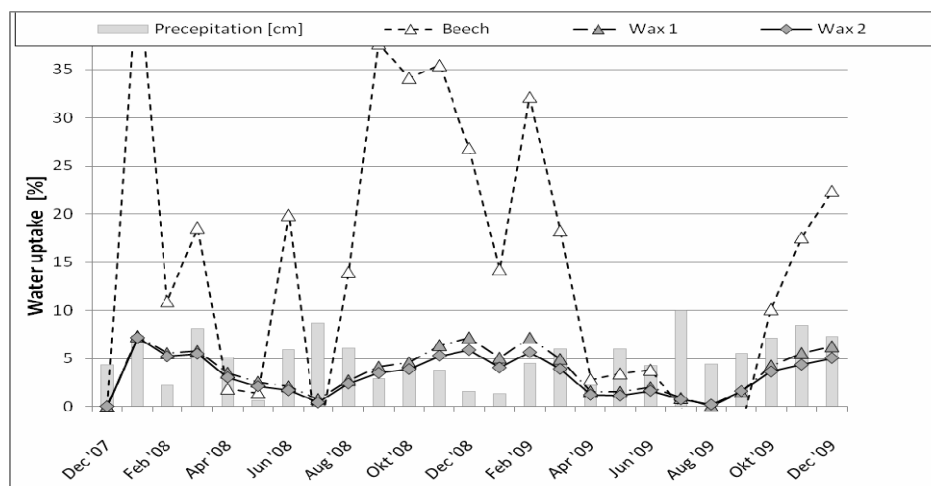


Figure 1: Water uptake of wax impregnated beech during two years of outdoor exposure

A correction by relating the water only to the original wood mass lead to a maximum mass increase of 19%. A permanent and significant lower water uptake of wax impregnated wood can be assumed.

Crack formation and stain penetration

Table 1 shows a similar frequency of cracks between references and treated specimens. Remarkable different are their broadness and deepness. Generally, wax impregnated beech has a higher dimension stability and finer cracks. Greying and staining is limited to the surface in contrast to native beech specimens (Figure 2).

Table 1: Evaluation of the cracks according to EN ISO 4628-4 (1997)^a

Parameter	Rank	Native beech	Wax impregnated beech
Frequency	0 – 5	5,0	2,5 .. 4,0 .. 5,0
Broudness	0 – 5	4,2	2,0 .. 3,0 .. 3,5
Deepness	0 – 4	2,8	1,0 .. 1,5 .. 2,0

^aDeepness is no parameter according to this standard and was therefore introduced



Figure 2: Specimens after two years of weathering. a) Surfaces of native beech. b) Cut references. c) Cut specimens of wax impregnated wood. d) Surface of impregnated beech with wax 1 and e) wax 2

Color evaluation

A rapid loss of lightness (-18%) was observed for native beech after three month as well as two years (-38%) of outdoor exposure (Figure 3). Besides a creation of phenolic compounds by solar radiation greying is caused by fungi colonization of the wood surface (Feist and Mraz 1978b). In contrast, the wax impregnated specimens became bright (27% wax 1; 14% wax 2) and showed a minor darkening (-6% wax 1; -24% wax 2) after two years. The better results are likely caused by various factors. Wax is able to block the leaching of chromophoric groups. On the other hand, the infestation and penetration by fungi could be more difficult due to the blocking of wood lumina. Furthermore, Fig. 1 indicates a permanent low humidity of wax impregnated specimens which lead to worse colonization conditions. The chroma decrease (-73% wax 1; -62% wax 2) is higher for wax impregnated beech than for native specimens (-59%). But under consideration of Figure 2 that did not mean a worse optical appearance.

CONCLUSIONS

Wax impregnated wood shows a similar frequency of cracks like native controls. But these cracks are smaller and situated on the surface compared to untreated wood. The influence of water penetration as well as stain infestation remains limited on the surface.

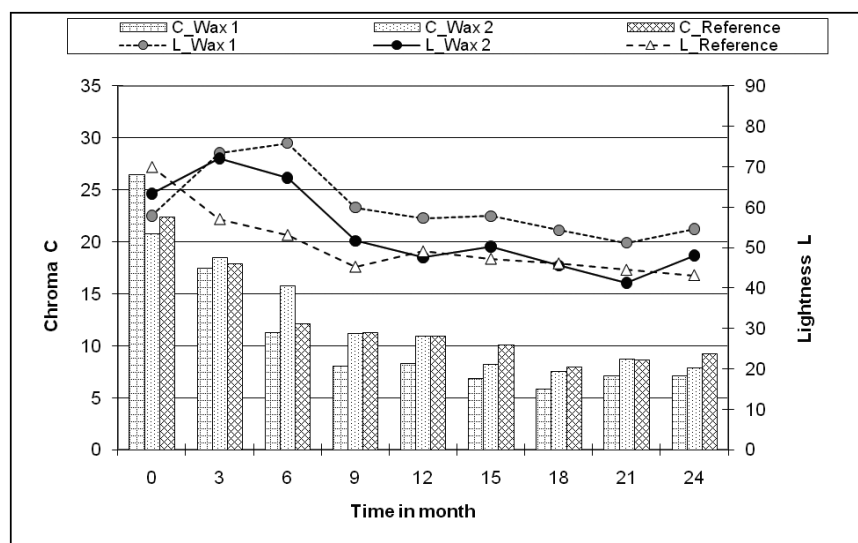


Figure 3: Changes of lightness and chroma of wax impregnated beech after two years

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A Preliminary Study into the Properties of Laminated Viscoelastic-Thermal-Compressed Wood

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Keywords: Brinell hardness, Densification, VTC

ABSTRACT

It is well known that wood can be compressed when above its glass transition point, without breaking the cell walls. Wood is a porous material and, in theory, can be rather easily compressed until the density reaches that of the cell wall material (~1.50 g/cm³). In this study, a viscoelastic thermal compression (VTC) method, which was developed at Oregon State University, USA, was used to modify the sapwood of 11-year old plantation hybrid poplar (*Populus deltoides* x *Populus trichocarpa* L.). Poplar specimens, initially 5mm in thickness, were first compressed to 1.5mm, resulting in an increase in density from 0.37 g/cm³ to 1.22 g/cm³. Subsequently, the VTC modified wood was laminated to untreated wood in order to create a composite laminate structure having high density surface and a low density core. The laminates were bonded using epoxy adhesive and either one or two layers of VTC wood, in order to produce specimens with different vertical density profiles. Surface hardness was measured using a modified Brinell hardness test; density profile was measured. The Brinell hardness method was modified, such that several loads were applied - 250N, 500N, 750N, 1000N, and 1250N, rather than a single load of 1000N as specified by the EN-1534 standard. The results show that the applied load has a significant influence on hardness. Hardness was found to have been increased significantly; the maximum value had been increased by more than 800%, from unmodified wood, when two layers of VTC wood were laminated to the unmodified wood and the applied load was 250N.

INTRODUCTION

It is well known that wood density correlates with its mechanical properties. It is possible to compress wood under certain conditions to increase the density. There are many methods for wood compressing. All different methods have same main phases, wood softening and wood compressing. One of the densification methods is called viscoelastic thermal compression (VTC). It was developed by Kamke and Sizemore (2008). The VTC process has wood softening phase above glass transition temperature (T_g) under saturated steam, followed by compression phase and heat-treatment and cooling (Kamke and Rautkari 2009; Rautkari *et al.* 2010). Several studies have shown that rather than densifying the entire bulk of a piece of wood, only the surface of solid wood can be densified (Rautkari *et al.* 2009a,b). One possibility to increase surface properties is compress bulk thin board and combine with untreated wood using an adhesive (Kutnar *et al.* 2008). The aim of this preliminary study was to use VTC process for compressing

wood and combine it with untreated wood. The density profiles and hardness values of these composites were measured.

EXPERIMENTAL

Wood material

The wood material was the sapwood of air dried 11-year old plantation hybrid poplar (*Populus deltoides* x *Populus trichocarpa* L.) with an average dry density of 0.37 g/cm³. Hybrid poplar was obtained from and northeastern Oregon (USA). Clear hybrid poplar specimens with tangential oriented growth rings were cut to 170 mm (longitudinal), 55 mm (tangential) and 5.5 mm (radial). All specimens were conditioned for at least 2 months in a conditioning chamber set at RH 65 % and 20°C, prior to compressing, which corresponds to equilibrium moisture content of 11.5 %.

VTC process

The wood densification was carried out in a reaction vessel where pressurized steam was delivered from a steam generator. The reactor incorporates separately heated platens with mechanical stops and a water cooling system. The vessel contains a LVDT (linear variable differential transformer) for measuring displacement and a load cell (50000 lbs = 220kN) for measuring applied load. The VTC process has several phases: wood softening, first-stage compression, venting, second-stage compression, heat-treatment, and cooling. The vessel was heated to 175°C and pressurized with saturated steam at 8.6 bar for 5 minutes, where the wood softening proceeds. A compressive force of 1.3 MPa was applied to the wood specimen for two additional minutes under steam pressure in the first stage compression. This phase was followed by venting steam out for approximately 30 seconds without compression. After moisture loss, the wood is compressed to the final desired thickness, in this study to 1.5 mm. Ultimately the wood is heat-treated by means of heated platens (175 → 200°C) without using steam and immediately followed by cooling phase, in which the material is cooled to under 100°C. The modified specimens were then glued using epoxy adhesive to untreated wood either a “single” layer of VTC wood or a “double” layer, more details are provided in an earlier report (Rautkari *et al.* 2010).

Hardness

Hardness measurements were conducted on an Intsrn 5582 testing machine equipped with a load cell of 10 kN and a 10 mm indenter. The hardness measurements were measured according EN-1534 (2000), but using different forces of 250N, 500N, 750N, 1000N and 1250N. The maximum indentation depth h was measured and not the diameter of the indentation, thus Brinell hardness H_B (N/mm²) was calculated using Eqn. 1. The maximum load was reached in 15 s. The force was maintained for 25 seconds and the load was released in 15 s.

$$H_B = \frac{F}{\pi * D * h} \quad (1)$$

where F is the applied force, D is diameter of the indenter, and h is the depth of the indentation.

Density profile measurements

The vertical density profile measurements were conducted using an X-ray densitometer (QMS, Model QDP-01). The specimens for density profile measurements ($50 \times 50 \text{ mm}^2$) were aligned cross-section up, which means that the X-ray attenuation occurred in the tangential direction and the density profile was measured with respect to the thickness (radial direction).

RESULTS AND DISCUSSION

Hardness

The preliminary results ($n=4$) of Brinell hardness of the laminated hybrid poplar with densified VTC wood are shown in Figure 1. The influence of the applied load and the thickness of the densified layer were examined. Moreover the hardness of untreated wood was measured. It is clearly seen that the applied force has a great influence on the hardness values, because as the indenter penetrates deeper the values are more representative of the properties of the wood beneath the densified surface. Moreover, the thickness of the surface laminations has great influence on the hardness values. This phenomenon is also exhibited by other composites such as particleboard (Niemz and Stübi 2000).

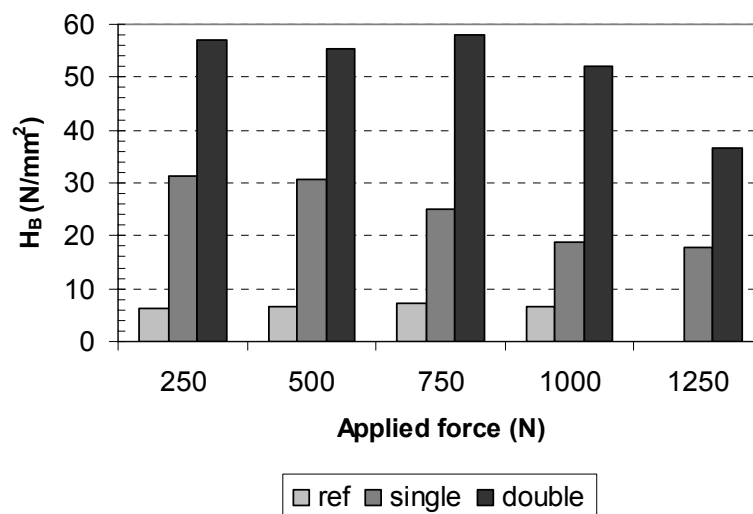


Figure 1: Brinell hardness of laminated hybrid poplar with single or double layers of densified wood; reference specimen is untreated hybrid poplar

Density profile

An example of a vertical density profile of laminated unmodified solid wood with high density densified wood surfaces is presented in Figure 2. The effect of lamination can be clearly seen; however, what is also of interest is the effect of the adhesive penetration and the densification of the untreated wood during clamping that can be seen in the right side of Figure 2. Manually measured density was 1.18 g/cm^3 , but the densitometer indicates approximately 1.25 g/cm^3 for the VTC wood, this difference is believed to be the result of the calibration process of the densitometer (Rautkari *et al.* 2010).

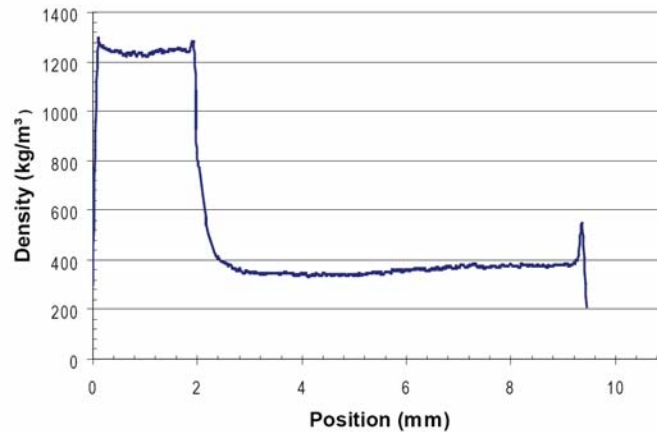


Figure 2: Density profile of laminated hybrid poplar with one layer of densified VTC wood

CONCLUSIONS

The surface properties of low density wood can be increased by lamination with densified wood. Hardness was found to have been increased significantly; the maximum value had been increased by more than 800%, from unmodified wood, when two layers of VTC wood were laminated to the unmodified wood and the applied load was 250N. The results show that the applied load has a significant influence on hardness.

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Condensation Process of Wood Impregnation

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Keywords: Atmospheric pressure, condensation, impregnation process, penetration depth, superheated steam

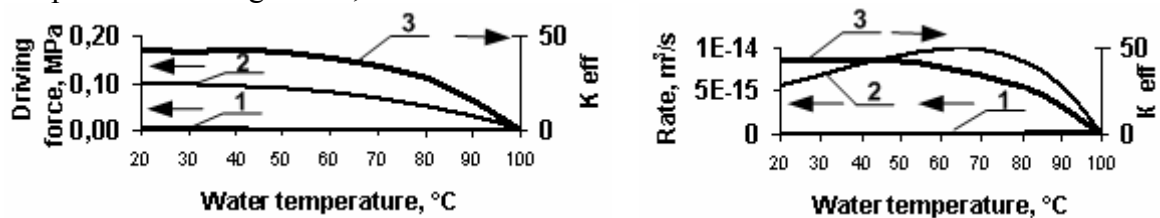
ABSTRACT

Method of intensification of the impregnation process at atmospheric pressure is used. Method is based on the replacement of air in the wood pores on steam phase, then immersion of wood in impregnating agent with temperature low, than condensation temperature. As a result steam is condensed in the wood pores and gets auto vacuum effect and it leads to the acceleration of impregnation and increase the penetration depth. Based on Hagen–Poiseuille equation of liquid flow in the pores driving force and the volume rate of flow in the ideal cylindrical glass capillary are defined. Condensation process (condensation impregnation) of incorporate into the capillary-porous wood volume coloured aqueous solution with the capillary process (capillary impregnation) under atmospheric pressure is compared. To compare the efficiency of the condensation impregnation efficient factor K_{eff} is used. The maximum efficient factors of condensation impregnation are in the range of water temperatures 20-50°C is demonstrated. Short series of experiments with saturated and superheated steam using (free convection and atmospheric pressure) for the condensation impregnation on the laboratory setup was carried out. Comparison of results with capillary impregnation was carried out. Method of visualization and quantification of the impregnation quality by coloured cross-section square and computer analysis of graphics information on histogram are suggested. Square of the impregnated wood section for 15 minutes for condensation impregnation was 87.1% at this time when the capillary impregnated square was only 10.1%.

INTRODUCTION

Recently, the wood modification becomes relevant in European countries, confirmation of this are regularly held European Conferences on Wood Modification in: Belgium (2003), Germany (2005), UK (2007), Sweden (2009), Latvia (2010). Worldwide most of the research work in wood modification technology focused on screening of potential chemicals and on testing wood properties. In Europe, recently, some of the most successful approaches (like acetylation, heat treatments, furfurylation, DMDHEU) were introduced to the market (Militz and Lande 2009). However, all methods of wood modification, except of thermal modification, make use of the impregnation stage in open tanks or under pressure. The process of mass liquid transfer in porous materials, subject to capillary wetting is called capillary impregnation (Frolov 1989). In our opinion the disadvantage of capillary impregnation in open tank is a shallow penetration depth, and lack of impregnation under pressure is using special equipment, in which the pressure is significantly different from the atmospheric (autoclave, vacuum pump, compressor) and it increases cost of wood modification technology. To solve these problems we used method of intensification of the capillary-porous materials

impregnation process (Zadorsky 2004), in particular for wood (Ghnilitskaya 2008, Zadorsky and Gnylytska 2009). Method is based on the replacement of air in the wood pores on steam phase, then immersion of wood in liquid impregnating agent. As a result steam is condensed in the wood pores and gets auto vacuum effect and it leads to the acceleration of impregnation and increase impregnation quality (penetration depth). Besides this condensation process of wood impregnation obviates the necessity for using of vacuum pumps, compressors, autoclaves, because any penetration depth can be achieved under atmospheric pressure. Based on Hagen-Poiseuille equation (Frolov 1989) driving force (Eqn. 1, Eqn. 2) and flow rate (Eqn. 3) in the ideal cylindrical capillary for capillary and condensation impregnation are determined. The driving force of capillary impregnation (Eqn. 1) is the difference from the capillary and the hydrostatic pressure in the capillary, for proposed condensation impregnation driving force (Eqn. 2) is the difference from atmospheric pressure of the liquid over capillary and the partial pressure of the liquid in the capillary. Calculations are made for capillary impregnation and condensation impregnation with water in the range of 20-100°C in ideal cylindrical glass capillary with radius $r=52 \times 10^{-6}$ m and length $l=0,05$ m, the results are presented on Figure 1 a,b.



1a. Impregnation driving force

1b. Impregnation rate

$$\Delta P_{capil} \text{ (MPa)} = P_{capil} - P_{hydr} \quad (1)$$

$$V \text{ (m}^3/\text{s)} = (\pi \times r^4 \times \Delta P) / (8 \times \eta \times l) \quad (3)$$

$$\Delta P_{cond} \text{ (MPa)} = P_{liq} - P_{part} \quad (2)$$

$$K_{eff} = \Delta P_{cond} / \Delta P_{capil} = V_{cond} / V_{capil} \quad (4)$$

Figure 1: 1 – capillary impregnation, 2 – condensation impregnation, 3 – efficient factor

Efficient factor (Eqn. 4) is the result of dividing of condensation impregnation driving force on the driving force of capillary impregnation (similar for impregnation rates). The calculations and plotted graphs (Figure 1, Figure 2) show that maximum driving force for condensation impregnation is observed at 20 °C ($\Delta P_{cond} = 0,0977$ MPa), maximum rates are in the range of 60-70 °C ($9,19-9,85 \times 10^{-15}$ m³/s), maximum efficient factors are in the range of 20-50°C ($K_{eff} = 41,71-42,48$), that is, the benefits of the condensation impregnation in comparison with capillary pressure become undeniable. Therefore short series of experiments which aimed to test the efficiency hypothesis of the condensation impregnation like increasing of penetration depth for a short time period under atmospheric pressure was carried out.

EXPERIMENTAL

Wood parallelepipeds 45x45x50 mm of pine (*Pinus sylvestris*) were processed. Experiments of condensation impregnation on laboratory setup were carried out (Figure 2). Laboratory setup consisted of steam generator 2 (3 l, $5,2 \times 10^{-4}$ kg/s), superheater 4, chamber 7 (cylinder $d=110$ mm, $h=275$ mm), laboratory autotransformer 5, K-type

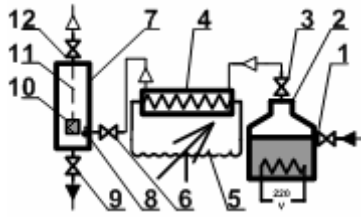


Figure 2 : Scheme of laboratory setup

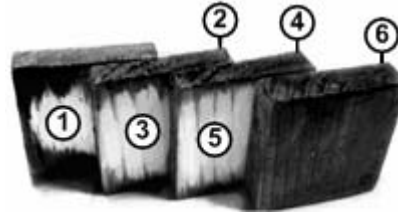


Figure 3 : Sample cross-sections

thermocouple 8. Valves 3, 6 and 12 were opened during all time of experiment. Sample 10 on thread 11 was hung through valve 12. Saturated steam under atmospheric pressure through valve 3 was entered in superheater 4, where it heated to the desired temperature, then it entered in thermally insulated chamber 7 through the valve 6, where sample 10 in free convection was heated, after that steam removed through the valve 12. After reaching specified steam treating time sample was removed from the chamber and immersed into open vessel with aqueous coloured solution at 20°C for 15 minutes. Then impregnated sample was removed from the vessel, wiped with dry cloth and sawed along the fibers into four equal parts (Figure 3). Further six coloured cross-sections were studied. Start of cross-sections numbering was from steam entrance into the chamber (Table 1, experiments #2-#4). Comparison of the results was carried out with the experiment, in which sample for 15 minutes immersed in an aqueous solution at 20 °C (capillary impregnation, Table 1, experiment #1).

RESULTS AND DISCUSSION

Typically, the penetration depth of substances, which have colour or pigmented wood cell after impregnating, is determined by the width of the painted area with a ruler. Penetration depth for capillary impregnation was 1-2 mm. But for condensation impregnation it was difficult to measure penetration depth using a ruler. And so method of analysis by coloured cross-section square on digital photos is suggested.

Table 1: Results of experiments

Experiment number	Steam temperature [°C]	Steam treating time [min]	Impregnation time [min]	Cross-section number											
				№1	S1,%	№2	S2,%	№3	S3,%	№4	S4,%	№5	S5,%	№6	S6,%
1	-	-	15		10,1		10,2		10,1		10,1		10,1		10,1
2	100	30	15		41,8		38,1		26,7		21,9		20		17,5
3	130	30	15		63,3		61		45,6		38,2		26,8		24,9
4	130	90	15		87,1		68,7		53,8		52,1		52		45,8

For example in Adobe Photoshop 7.0 determine spread of colours in coloured area with *Eyedropper* or *Colour Sampler* tool for determine *Tolerance* parameter of *Magic Wand* tool, select this area and fill in Black colour. Display histogram (Channel Luminosity).

Put pointer on the column in the left side of histogram. Register *Percentile* data. In our case it is square of impregnated cross-section S [%]. Digital photos of cross-sections and results of histogram analysis are shown in Table 1. *Qualitative estimation* of photos indicates that with rising in steam temperature and steam treatment time coloured square is rising too. Quantitative estimation (*e.g.* for cross-section #1) indicates, that for capillary impregnation for 15 min without steam treatment square $S_1=10,1\%$, for condensation impregnation: with using of saturated steam (for 30 min) $S_1= 41,8\%$, with using of superheated steam (for 30 min) $S_1= 63,3 \%$ and with using of superheated steam (for 90 min) $S_1=87,1 \%$. However, if optimal parameters of steam temperature, time steam treatment, steam flow and impregnation time are selected then impregnated square can reach 100% (straight-through penetration depth on the entire volume of any sample dimensions) under atmospheric pressure.

CONCLUSIONS

Thus, the hypothesis, based on theoretical calculations has been proved on practice. Method of impregnation quality analysis for wood impregnation with colouring liquid is proposed. It is convenient in case when penetration depth of liquid is difficult to measure with a ruler. However experiment was aimed at acceleration of capillary impregnation with aqueous solution and increasing the penetration depth for a short time period under atmospheric pressure without investigation of chemical and physical-mechanical characteristics of wood. So for development of studies at research level it is necessary to evaluate the influence of thermal treatment with superheated steam-condensation impregnation with aqueous modifying agent-drying with superheated steam on chemical, physical and mechanical properties of different wood species. If positive results are achieved, the next step will be up-scaling and full-scale for commercializing proposed impregnation technology taking into account the synergistic effects of combining stages of heating, impregnation and drying in one multifunction unit. It significantly will reduce capital investment (obviates the necessity for using of vacuum pumps; compressors; autoclaves; interoperable transport operations), reduces the production area and speed up the process of wood modification in general.

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Screw and Nail Withdrawal Resistance of Some Heat-treated Woods

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Keywords: Heat treatment, wood, nail, screw, withdrawal resistance

ABSTRACT

In this paper, the effect of heat treatment on screw and nail withdrawal resistance of Scotch pine (*Pinus sylvestris* L.), oriental beech (*Fagus orientalis* Lipsky.), fir (*Abies nordmanniana* subsp. *bornmülleriana* Mattf.) and poplar (*Populus canadensis*) woods were determined and compared with control specimens. Heat treatment conducted under atmospheric pressure with nitrogen gas at three different temperature (120, 160 and 200°C) and two different time levels (2 and 6 hours). According to results, maximum nail withdrawal resistance values were obtained for oriental beech at radial surface at 120°C for 6 h as 1332 N. For all wood types, screw WR decreased with increasing the treatment temperature and increasing treatment time didn't affect significantly ($p < 0.05$) on screw WR.

INTRODUCTION

Fastening elements are important for the stability of any building system, composed of interconnected components. This is directly related to the performance of the fastening elements. Nails and screws are the most widely used fastening elements of solid wood materials. Therefore, for wooden building elements, knowledge of the withdrawal resistance of nail and screw will provide useful information about the durability and stability of the whole system (Celebi and Kilic 2007). The wood material maintains its significance in many fields of use today due to its superior features. But it also suffers a number of disadvantages. The wood material wears out as dependent on the environmental conditions such as water, sun beams, rain and snow. In order to ameliorate these disadvantages and to extend its economic life, it is subjected to some processing such as impregnation by means of various chemical materials and heat treatment methods. Heat treatment processes are used to modify the properties of wood (Mazela *et al.* 2004). Wood polymers are degraded and color darkens (Ates *et al.* 2009, Akyildiz *et al.* 2009a, Akyildiz *et al.* 2009b, Ates *et al.* 2010), dimensional stability is enhanced, equilibrium moisture content is lowered (Akyildiz and Ates 2008), and biological durability is increased (Hill 2006). The main objective of this study is to determine effect of heat treatment on screw and nail withdrawal resistance of Scotch pine (*Pinus sylvestris* L.), oriental beech (*Fagus orientalis* Lipsky.), fir (*Abies nordmanniana* subsp. *bornmülleriana* Mattf.) and poplar (*Populus canadensis*) woods.

MATERIALS AND METHOD

Scotch pine (*Pinus sylvestris* L.), oriental beech (*Fagus orientalis* Lipsky.), fir (*Abies nordmanniana* subsp. *bornmülleriana* Mattf.) and poplar (*Populus canadensis*) were

used as wood materials in the test specimens. Wood materials were obtained from forest lands of the Kastamonu province, Turkey. The wood materials was cut in parallel to grain directions from the logs in sawmill and then small clear specimens were cut for tests. For nail and screw withdrawal resistance, the specimen with dimension 50x50x150 mm were prepared according to TS 6094 and ASTM-D 1761. Heat treatment applications of specimens were performed in an oven under nitrogen atmosphere. The treatment started by putting the samples at ambient temperature in the oven, and the period to reach the treatment temperature was about 1 hour for all trials. Three different temperatures (120, 160 and 200°C) and two different durations (2 and 6 h) were applied to specimens under atmospheric pressure. After treatment, the temperature is decreased to room temperature that takes about 24 hours. The same procedure was conducted for all experiments. After the heat treatment, the specimens were left at 20°C and 65% RH for 8 weeks and screws and nails driven and then were tested. Screws were driven in the pilot holes drilled on the face of the specimens. Total 6 nails and 6 wood screws for each sample were used for withdrawal tests. Nail dimensions were 2.5 mm diameter and 50 mm length, flat-head wood screw dimensions were 4.5 mm diameter and 50 mm length. Withdrawal tests were carried out according to the procedure of ASTM-D 143-94 and TS 6094 standards. The loading speed was 2.5 mm min⁻¹ for nails and screws. The loading was carried on until a separation occurred on the screw or nail of the test samples. The values reading maximum power on test machine were recorded as withdrawal resistance of the samples.

RESULTS AND DISCUSSIONS

Although screw withdrawal resistance (WR) for transverse surfaces were found as the lowest, WR for radial surfaces were highest for all wood types. Because similar tendencies have been obtained for all surfaces (transversal, tangential and radial), results for only radial surfaces were discussed in this paper. Results of screw withdrawal resistance for radial surface of each wood type are presented in Figure 1.

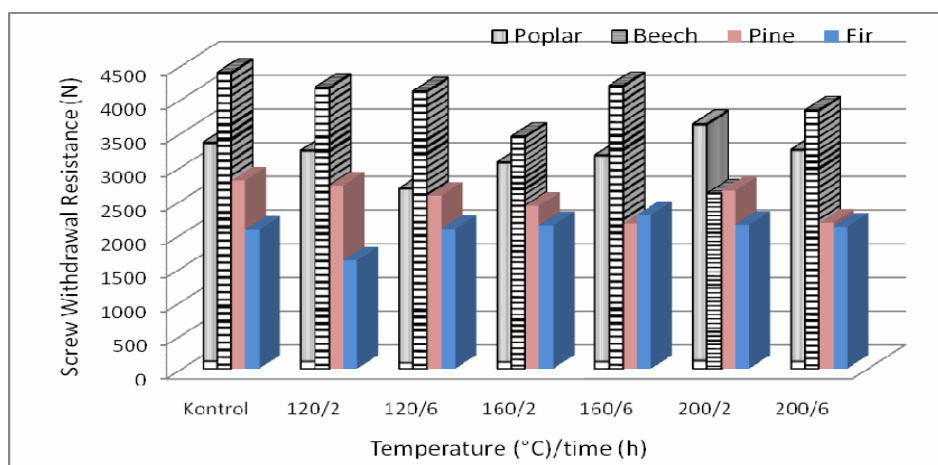


Figure 1. Screw withdrawal resistance for radial surface of each wood type

As can be clearly seen from Figure 1 that deciduous wood types have higher withdrawal resistance (WR) than conifer wood types. Beech gave the highest screw WR. Possible reason of this, specific gravity of beech is higher than the others. Because holocellulose content changed negatively with increasing temperature and time (Ates *et al.* 2009, Akyildiz *et al.* 2009a, Akyildiz *et al.* 2009b, Ates *et al.* 2010) for all wood types, WR

decreased with increasing the treatment temperature. According to statistical analysis (ANOVA), it was determined that increasing treatment time didn't affect significantly ($p < 0.05$) on screw WR. For radial surfaces, the maximum screw WR reduction rates were obtained for beech, pine, fir and poplar as 40.8%, 22.8%, 22.2% and 20.3% compared with the control sample, respectively. Results of nail withdrawal resistance for radial surface of each wood type are presented Figure 2.

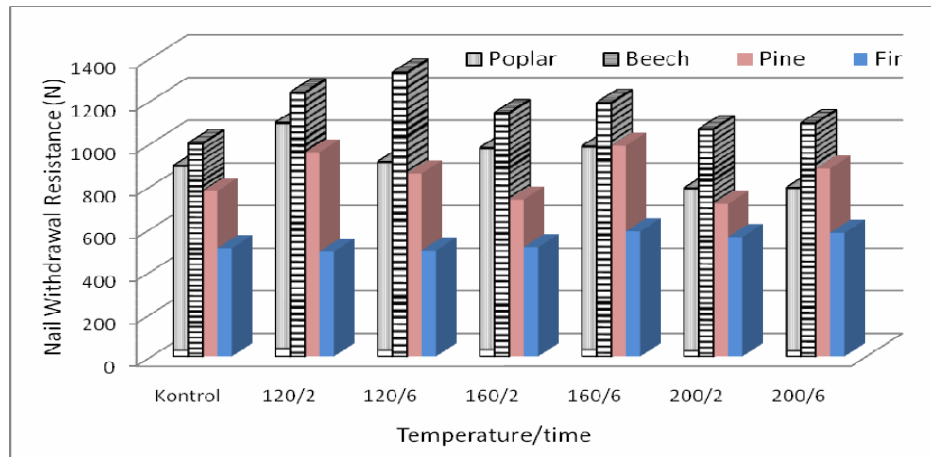


Figure 2. Nail withdrawal resistance for radial surface of each wood type

As can be seen from Figure 2 that deciduous wood types have higher WR than conifer wood types similarly with nail WR. Beech gave the highest nail WR. It can be explained with higher specific gravity and special anatomic properties of beech. Since shrinkage of wood volume by drying and tightening of anatomical wood structure, nail WR increasing with both treatment temperature and time. Statistical analyses (ANOVA) confirms these results ($p < 0.05$). Although, total loss in nail WR were recorded for poplar as 11.8% at the treatment of 200 °C for 2 h, the maximum increasing rates were found as 33.2%, 27.4%, 22.6% and 15.6% for beech, pine, poplar and fir compared to the control sample, respectively.

CONCLUSIONS

The principal conclusions of this study are summarized below.

- Screw withdrawal resistance have decreased with increasing treatment temperature however increasing treatment time didn't affect significantly ($p < 0.05$) on screw WR.
- Nail withdrawal resistance have increased with increasing both treatment temperature and time.
- Among the surfaces, the maximum screw and nail withdrawal resistance values were determined at radial surface however the minimum values were obtained at transversal surface for all experimental conditions.
- According to these results, utilization of screws and nails for longitudinal connections should be avoided. Although screw withdrawal resistance has decreased with increasing heat treatment temperature and time for all wood species, as fastening materials for heat treated wood screw using will be better instead of nail.

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Pilodyn Testing of Thermally and Chemically Modified Wood

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Keywords: Chemical wood modification, heat treatment, maritime pine, Pilodyn, *Pinus pinaster*, resistance to impact milling

ABSTRACT

Two methods were used to test modified wood: determination of the penetration depth of a Pilodyn 6J tester and the resistance to impact milling (RIM). Various types of modified wood were tested: Maritime pine (*Pinus pinaster*) was heat-treated and chemically modified with N-methylol melamine, wax (montan and amid wax), 1,3-dimethylol-4,5-dihydroxyethyleneurea (DMDHEU), and tetra-ethoxysilane (TEOS). European beech (*Fagus sylvatica*), Blue gum (*Eucalyptus globulus*) and Ipê (*Tabebuia serratifolia*) were included in the study as a control untreated hardwood species. With regard to heat treated wood, the penetration depth of the Pilodyn correlated well with the weight loss due to thermal degradation. When untreated wood was compared, the penetration depth decreased with increasing density of wood. The penetration into untreated pine wood increased with increasing moisture content up to the fibre saturation point and was constant above. Chemical modification decreased the penetration depth by 25-50% as compared to untreated pine wood, regardless of the density obtained. Penetration depth in modified wood was the same in early and late wood. Determination of RIM resulted in low particle sizes in case of heat treated wood, while untreated and chemically modified specimens yielded in big particle as the main fraction. The RIM correlated with the weight loss of the wood specimens after heat treatment. In the case of chemically modified specimens any correlation was found between RIM and Pilodyn hardness.

INTRODUCTION

The Pilodyn 6J is a portable tool which can be used for rapid and non-destructive assessment of wood density from living trees and timber. It can also detect biological decay of wood, e.g. soft rot in poles (Watt *et al.* 1996). The RIM factor assesses the destruction level of small specimens crushing by thousands of impacts with steel balls in a vibratory mill (Rapp *et al.* 2006). The two methods were used because they are simple to perform in order to characterise the effects of modification and of biological decay of wood.

EXPERIMENTAL

Material and Method

Maritime pine (*Pinus pinaster* Ait.) sapwood blocks (r x t x l - 60 x 30 x 150 mm³) was heat treated and chemically modified with N-methylol melamine, wax (montan and amid), 1,3-dimethylol-4,5-dihydroxyethyleneurea (DMDHEU), and tetra-ethoxysilane

(TEOS) as described previously (Militz 1993, Epmeier *et al.* 2004, Donath *et al.* 2004 and Scholz *et al.* 2010). The heat treatment was performed with heated air at 180 and 200°C in an oven for 3, 8, 15 and 24 h. Untreated Blue Gum (*Eucalyptus globulus* Labil.), European Beech (*Fagus sylvatica* L.), Ipê (*Tabebuia serratifolia*(Vahl) Nich) served as reference species to assess the effect of hardness on the Pilodyn test and on RIM. The Pilodyn test was performed using a Pilodyn 6J (Proceq 2003). Resistance to impact milling (RIM) was carried out as described by Rapp *et al.* (2006). The specimens were conditioned at app. 22°C and 65% RH. A full cell impregnation process with water was performed at 700 mbar (30 min) and 12 bar pressure (2 h) to establish water saturation. Ten replicates were used per treatment and species.

RESULTS

Effect of density, moisture content and heat treated wood on Pilodyn testing

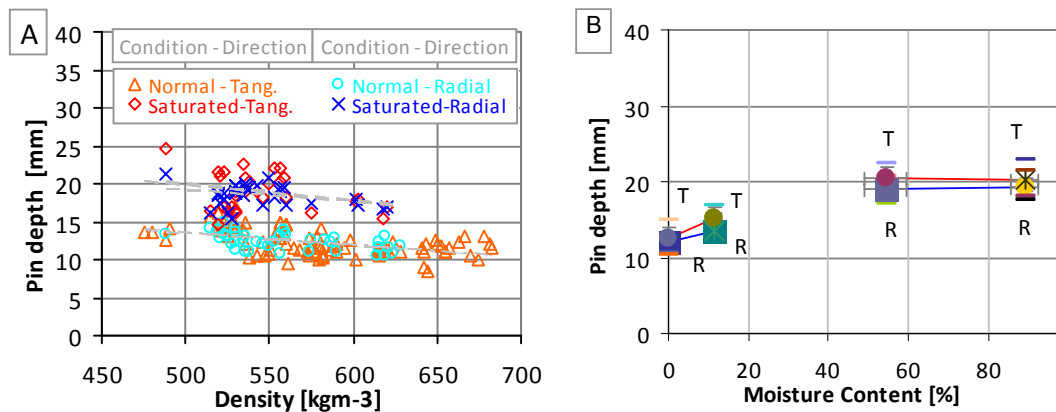


Figure 1: Penetration depth of Pilodyn 6J (with 2.5 mm blunt pin) into *Pinus pinaster* in radial and tangential direction. [A] Influence of natural density, for normal (65% RH, 22°C) and water saturated condition. [B] Influence of moisture content on penetration depth (n = 10).

The penetration depth of Pilodyn 6J tended to decreased with increasing density of the wood species tested (Figure 1A). For pine wood, the penetration depth varied between 10 and 17 mm; this corresponds to one or two up to nine or ten annual growth rings per cm depending on the wood texture. The pin penetration increased with increasing moisture content up to the fibre saturation point and was constant above (Figure 1B).

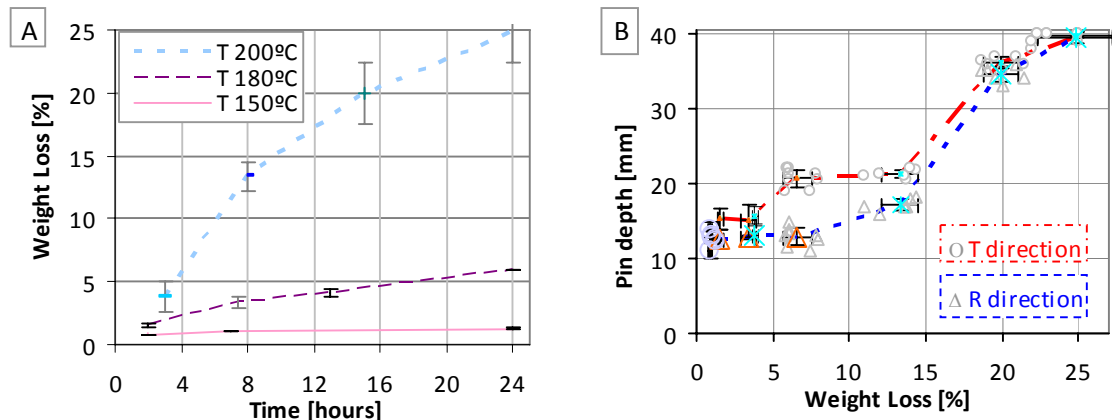


Figure 8: [A] Weight loss of pine wood blocks after different exposure times at 150, 180 and 200°C. [B] Penetration depth of Pilodyn 6J related to the weight loss due to heat treatment in radial and tangential direction (n = 10)

During heat treatment, the wood specimens continuously lost their weight due to thermal degradation. The highest weight loss of approximately 25% was observed after 24 h exposure at 200°C (Figure 2A). The radial penetration of the Pilodyn pin was deeper than the radial one (Figure 2B). The penetration depth increased with increasing weight loss of the wood specimens due to thermal degradation.

Pilodyn testing of chemically modified wood

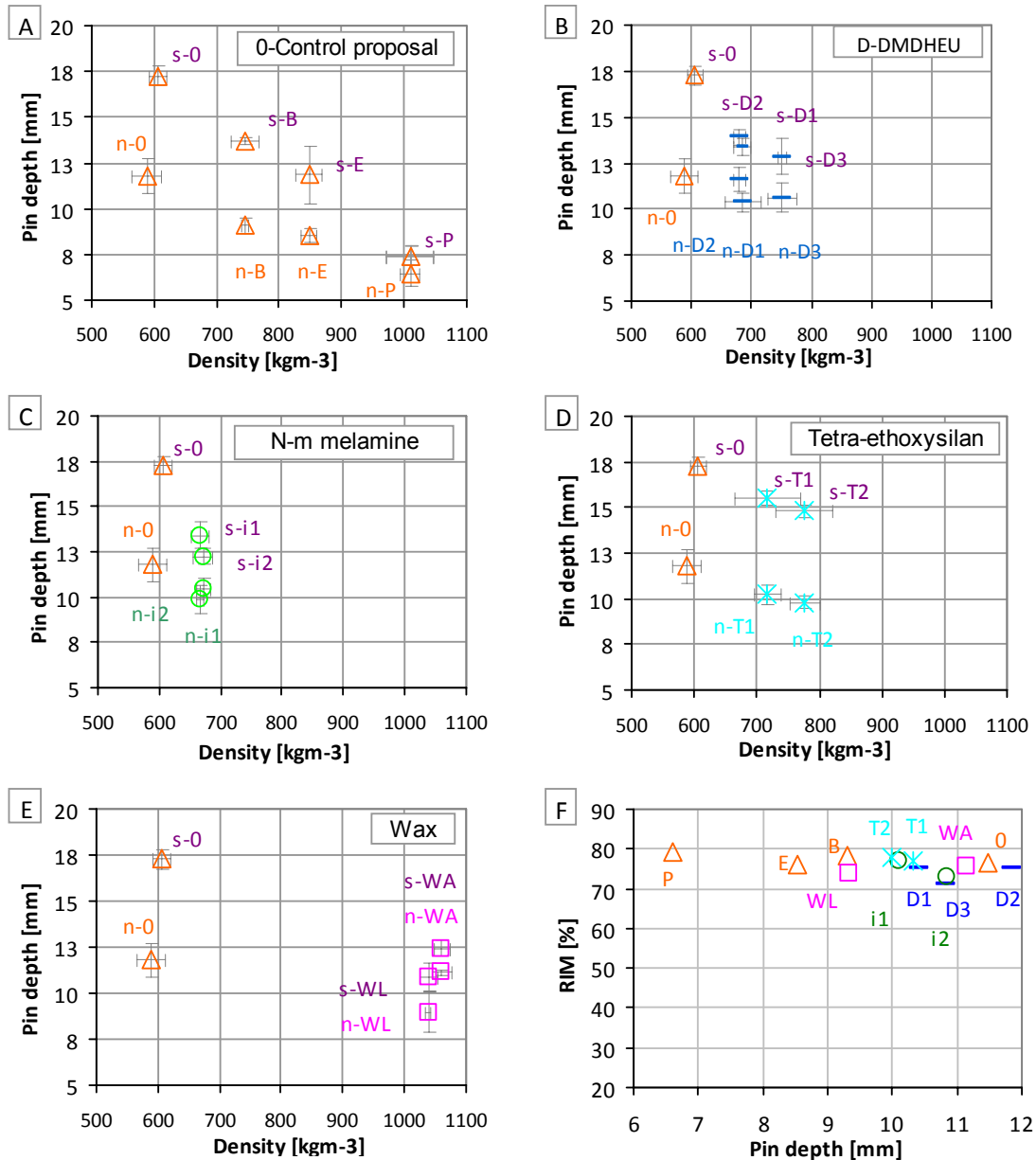


Figure 9: [A-E] Penetration depth of Pilodyn in wood related to the density of chemically modified wood (n: normal (65% RH, 22°C), s: water saturated condition). A: untreated wood species: Blue Gum –E, Beech-B, Ipê-P, pine-O); pine wood modified with [B] DMDHEU (D1, D2, D3), [C] N-methylol-melamine (i1: 16%,i2: 38% WPG), [D] tetra-ethoxysilan (T1, T2), [E] wax (WL montan, WA amid); [F] correlation between RIM and the penetration depth of Pilodyn.

When four untreated wood species (Pinus, Beech, Blue gum and Ipê) were compared, the penetration depth of the Pilodyn decreased with increasing under normal (20°C/65% RH) and water saturated conditions (Figure 3A). Increased density due to chemical

modification (DMDHEU, N-methylol-melamine, TEOS, wax) also resulted in lower penetration depth (Figure 3B-E).

In wood modified with DMDHEU, N-methylol-melamine, and wax the Pilodyn penetration into the water saturated specimens was approximately 2 mm deeper than under normal moisture conditions, except for TEOS where it was 5 mm. A correlation of the penetration depth of the Pilodyn and the RIM factors of chemically modified wood specimens could not be found (Figure 3F).

CONCLUSIONS

The Pilodyn is a valuable tool for a quick and low cost-effective assessment of the wood density. Determination of the penetration depth provides reasonable correlations with the density as well as the weight loss due to wood degradation by heat. The determination of RIM did not provide any valuable results because the impact during ball milling was too low to destroy untreated or chemically modified wood and to produce smaller fraction.

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Thermogravimetric Analysis of Heat Treated Spruce Wood – a Possible Tool for External Quality Control?

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Keywords: Quality control, spruce, thermal treatment, thermogravimetry

ABSTRACT

Several thermogravimetric calibration curves, representing the mass losses in a certain temperature range, compared to mass losses caused by previous heat treatment (known values), were established for spruce wood samples, modified in a process with initial vacuum at different isothermal temperatures (from 170 to 220°C). A linear plot with the highest correlation factor ($R^2 = 0.96$) was obtained for the TG mass losses from 130 to 300°C under nitrogen atmosphere. The predominant cause of mass loss in this temperature range was depolymerisation and thermal decomposition of hemicelluloses residues. Since modified wood exhibits lower affinity to water (higher modification degree, lower affinity) a dehydration process of pre-equilibrated samples from room temperature up to 130°C could also give good (exponential) correlation between modification degrees and observed mass losses. Besides that, the dehydration step is not dependent on the type of the atmosphere used during the thermogravimetric measurement. The results of this work show that thermogravimetry could be a useful tool for external quality control of heat treated spruce wood.

INTRODUCTION

Thermogravimetry (TG) and differential scanning calorimetry (DSC) as complementary methods of thermal analysis were used in the past for a variety of studies made on wood. In the article written by Nguyen and co-workers, thermal analysis of lignocellulosic materials is reviewed in 185 references (Nguyen *et al.* 1981). Since there is a lack of a simple and established external method for controlling a degree of heat treatment (HT), the purpose of this study was to find a reliable calibration curve, representing mass loss in a certain temperature range, obtained from TG curves, compared to mass loss observed during previous heat treatment (known values). A set of spruce wood samples, heat treated in a temperature range from 170 to 220°C, was investigated.

EXPERIMENTAL

Wood blocks (dimensions $t \times r \times l$: 20 mm \times 20 mm \times 10 mm) of the same Norway spruce (*Picea abies* (L.) Karst) pole were isothermally treated for three hours at 170, 180, 190, 200, 210, and 220°C, respectively. A description of HT procedure with initial vacuum has been published elsewhere (Rep *et al.* 2004). Five wood blocks were prepared for each process (temperature). The samples were first oven-dried at $103 \pm 2^\circ\text{C}$

for 12 h and weighted before and after the heat treatment. The mass losses of dry specimens varied from 0.52% (after treatment at 170°C) to 8.58% (after treatment at 220°C). After heat treatment, the blocks were milled and sieved to obtain particles smaller than 1 mm. Five untreated samples were also examined. Dynamic thermogravimetric measurements in temperature range from 25 to 600°C were performed on a Mettler Toledo TG/SDTA 851^e instrument under a dynamic nitrogen flow with a flow rate of 100 mL min⁻¹. Heating rate was 5 K min⁻¹, while initial masses of the samples were around 10 mg. A baseline was subtracted in all measurements.

RESULTS AND DISCUSSION

Deterioration of hemicelluloses already begins at or below 180°C (Sivonen *et al.* 2002). The minimum temperature for the decomposition of cellulose crystals in an inert atmosphere is considered to be between 300 and 360°C (Kim *et al.* 2001). Lignin exhibits high structural diversity and degrades gradually over a wider temperature range than carbohydrates (Alén *et al.* 1995). TG curves of wood samples, heat treated to a different degree, are presented in Fig. 1. For clarity, only four are represented. In the first step, from room temperature up to 130°C, a dehydration process takes place. The amount of rehydrated water depends on the degree of previous heat treatment (Fig. 2). Correlation between the amount of rehydrated water and the mass loss during heat treatment is exponential (Fig. 3).

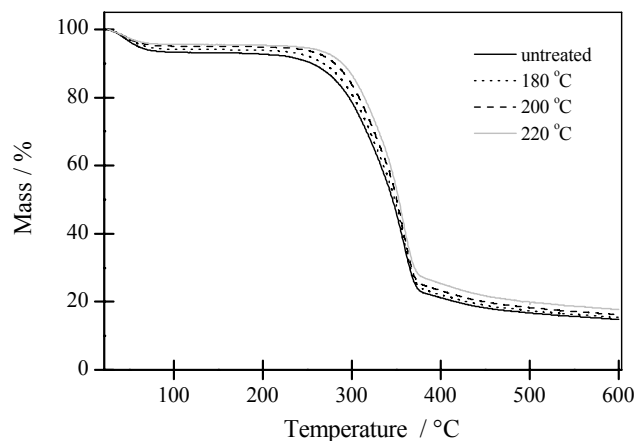


Fig. 1: TG curves of untreated and heat treated spruce wood samples

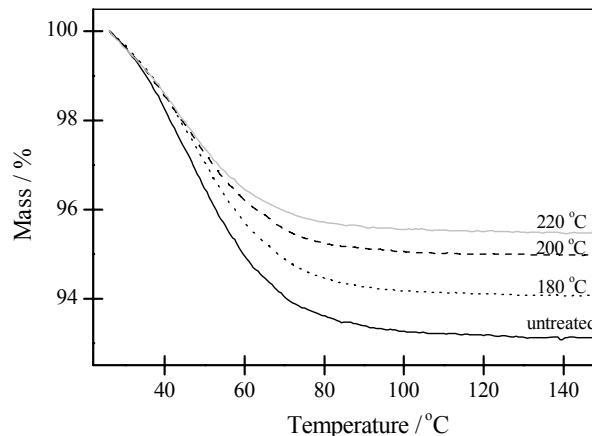


Fig. 2: Magnification of the mass loss curves in the temperature range from 25 to 150°C

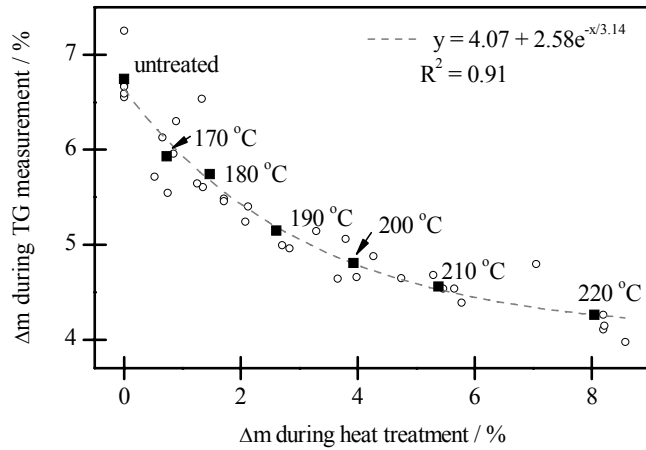


Fig. 3: A calibration curve for a TG range from 26 to 130°C; circles represent each individual sample, while filled squares calculated average values for each isothermal HT temperature

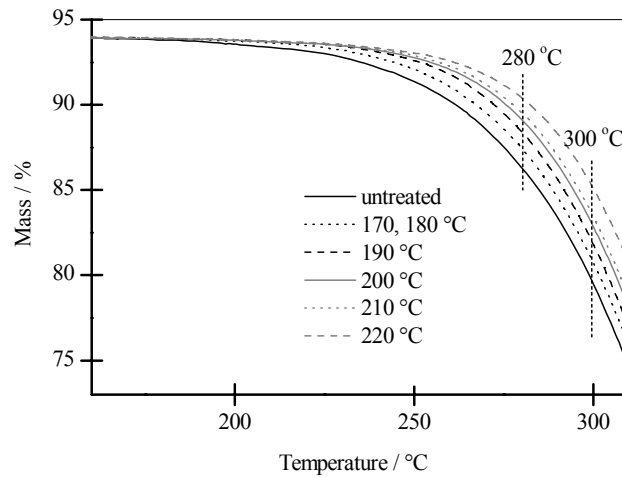


Fig. 4: TG curves of the wood samples in the temperature range from 160 to 310 °C; all curves were put at the same starting point at 130°C

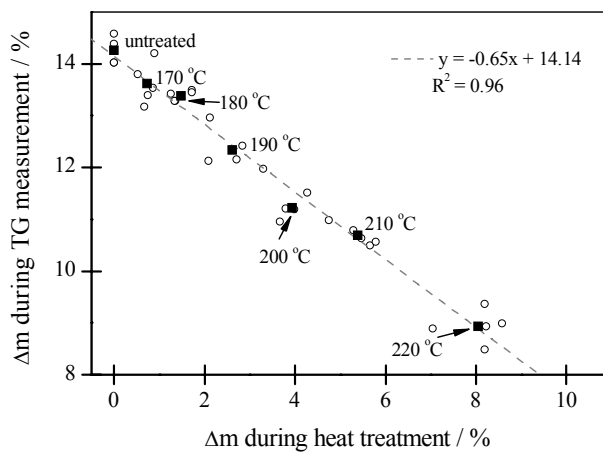


Fig. 5: A calibration curve for a TG range from 130 to 300 °C; circles represent each individual sample, while filled squares calculated average values for each isothermal HT temperature

At higher temperatures (>200°C) in nitrogen atmosphere thermal decompositions, which had not been completed during previous heat treatment, continued. In the temperature range from 200 to 310°C, samples modified to a higher degree exhibited lower mass losses, and *vice-versa*. From 280 to 300°C there is a maximal difference in the mass loss between untreated samples and samples treated (modified) to the highest degree (Fig. 4). A calibration curve with the highest correlation coefficient was observed for the temperature range from 130 to 300°C (Fig. 5). Correlation coefficients of calibration curves calculated for wider temperature ranges were much lower.

CONCLUSIONS

Thermogravimetry could be a useful tool for determination of the modification degree of heat treated spruce wood samples. The obtained results showed that there was a different amount of rehydrated water (different equilibrium moisture content) and a different content of hemicelluloses and/or hemicelluloses residues in spruce wood samples, which were isothermally modified for three hours at 170, 180, 190, 200, 210, and 220°C, respectively. In the TG temperature range where calibration curve with a highest correlation coefficient was observed (130 to 300°C), depolymerisation and thermal decomposition of hemicellulose was the predominant reason for the mass loss. However, to confirm thermogravimetry as a reliable tool for the external quality control of heat treated wood, further investigations with larger statistical population of representative samples will be needed.

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Covalently Attached UV-absorbers for Improved UV-protection of Wood

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Keywords: UV-protection, UV-absorbers, epoxy functionalized vegetable oils, grafting

ABSTRACT

The present study describes the use of reactive UV-absorbers (UVAs) that can be covalently attached to a wood substrate to obtain an improved exterior durability. It has previously been demonstrated that the photostability of wood is increased if the UVA is grafted to the wood surface. The grafting of an epoxide-functional UVA, 2-hydroxy-4(2,3-epoxypropoxy)-benzophenone (HEPBP), to thin veneer wood specimens had a larger photostabilizing effect than if the corresponding UVA without the reactive handle was added to the wood coating. The present study shows that not only the chemical structure of the UVA is important but also how the modification is performed i.e. the reaction procedure. A successful attachment of the UVA depends on both the reaction conditions as well as if other reactive species are present at the same time. The presence of for example a vegetable oil (epoxy functionalized soy bean oil) affects the grafting reaction of the UVA. Details on the effect of reaction conditions, reaction sequences, and presence of co-reactants will be presented.

INTRODUCTION

Wood is an attractive and renewable construction material. It does, however, suffer from drawbacks; it is moisture sensitive and the lignin absorbs UV light, which induces chemical degradation. UV absorption of lignin has a dramatic effect on the wood properties and wood for exterior use needs proper protection in order to be durable. Traditionally, this has been achieved by hiding the lignin under pigments in the wood coating, which hinders the UV light to reach the lignin. Due to an increased demand for clear-coated wood in exterior applications new alternatives need to be developed. A common protection method for wood is the pre-treatment with water soluble inorganic salts, such as CCAs, which protects the wood but where major disadvantage with the method is the negative impact on the environment which increases the demand for an alternative treatment. A more environmentally friendly and remaining method is UV protection through the addition of photostabilizers or UV absorbers (UVAs) to the wood coating system. Mixing of UVA into the coating can initially improve UV protection, but the efficiency decreases over time, due to leaching. It has recently been demonstrated that the photostability of wood is largely increased if the UVA is grafted to the wood surface, i.e. covalently linked. Kiguchi and Evans (1998) and later Westin (2002) also showed that the grafting of an epoxy-functional UVA, 2-hydroxy-4(2,3-epoxypropoxy)-benzophenone (HEPBP), to thin veneer wood species had a larger

photostabilizing effect than if the corresponding UVA without the reactive handle was added to the wood coating. Furthermore the grafted wood shows less discoloration than when treated with CCAs. Vegetable oils are renewable materials that cure through an oxidative mechanism to form clear cross-linked coatings. However, oxidative curing continues throughout the lifetime of the coating, resulting in reduced service life. One way to encounter this problem is to change the functionality of the fatty acids, *e.g.* with epoxide groups, that can be cured through other mechanisms. A benefit with the epoxy functionalized vegetable oils is their increased ability to react with the wood surface and form covalent bonds, which can result in improved adhesion to the substrate. The aim of this study is to combine the epoxy functionalized vegetable oils with reactive UVAs to obtain a nearly 100% renewable wood primer that makes clear-coated exterior wood more durable. Due to the similar chemistry of the two substances, UVA and epoxy groups, it is also possible that copolymerization will occur.

EXPERIMENTAL

HEPBP synthesis

First the reactive UV-absorber 2-hydroxy-4(2,3-epoxypropoxy)-benzophenone (HEPBP) was synthesized from reacting 2,4-dihydroxy-benzophenone (DHBP) and epichlorohydrin in 2N (0,2 mole/dm³) KOH at 80°C for 2 h. A yellow substance was produced and washed 6 times with deionized water and the excess solvent was evaporated under reduced pressure. The product was recrystallized 3 times with ethanol resulting in a yellow crystalline powder. (Manasek *et al.* 1976)

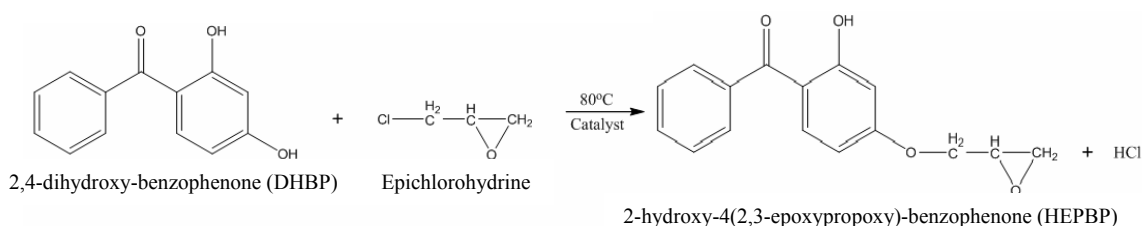


Figure 10: Synthesis of HEPBP from DHBP and epichlorohydrine

Veneer manufacture

The veneers used were produced from pine and spruce blocks (1 × 2 cm) which were placed in water for a minimum of 24 h prior to cutting. The blocks were cut with a microtome (Reichert, No. 11519) and a veneer thickness of 90 μm was used. After cutting, the veneers were wet again and dried between two glass plates in an oven at 105°C over night to flatten the veneers.

Grafting of wood veneers with HEPBP and/or epoxy functionalized soybean oil

In the initial experiments veneers of pine and spruce (1 cm × 2 cm × 90 μm) were prepared and extracted in a mixture of acetone/ethanol (2:1) at 90°C for 8 h using soxhlet extraction. Veneers were then dried in an oven at 105°C over night. The extracted veneers were weighed separately and then put in a round bottom flask into which 150 ml acetone, 2.0 g of HEPBP (or epoxy functionalized soybean oil) and 0.2 g of 4-(dimethylamino)pyridine (DMAP) was added. For modifications with both HEPBP and oil 1.0 g of each was used. The mixture was left to react at 120°C for 16 h and was then extracted for 24 h using soxhlet extraction. Veneers were then re-weighed and analyzed by IR to determine if reaction had occurred.

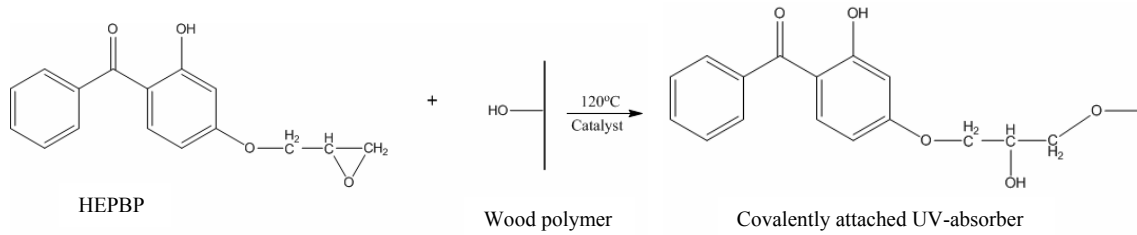


Figure 11: Grafting reaction between HEPBP and wood

QUV

By exposing the veneers to ultraviolet light (UV light) and water condensation in a QUV it is possible to perform accelerated weathering tests of the veneers. In this trial the veneers were exposed to 608 h of UV light in 24 h cycles consisting of 16 h of UV light followed by 8 h of condensation. Approximately every 60th UV-hour colour measurements were made and the results were plotted as in Figure 3.

FTIR

To analyze the veneers ATR-FTIR (Attenuated Total Reflection-Fourier Transform Infrared Spectroscopy) was used. The equipment used was a Perkin-Elmer Spectrum 2000 FT-IR equipped with a MKII Golden Gate, Single Reflection ATR System from Specac Ltd., London, U.K. The ATR crystal was a MKII heated Diamond 45° ATR Top Plate.

RESULTS AND DISCUSSION

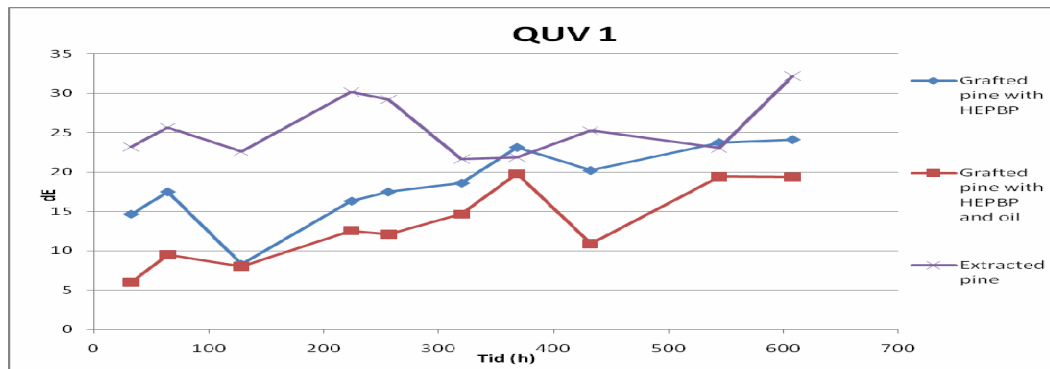


Figure 12: Colour changes for veneers during UV exposure in QUV

The analyses from the initial experiments show promising results. In the FTIR spectrum several peaks (e.g. 625, 1111, 1258 and 1576-1620 cm^{-1}) suggests that the HEPBP has reacted with the wood substrate, which is similar to results from previous experiments (Kiguchi and Evans 1998). Due to the complicated IR spectrum of the HEPBP the oil has unfortunately been difficult to identify but by studying the veneers in contact with water it is possible to say that the oil has turned the wood surface more hydrophobic. Another property that indicates reaction between HEPBP and wood is that the veneers after reaction have gained a slightly yellow colour which stays even after extraction for 24 hours. Although reaction seems to have occurred the veneers were too small to result in any weight gain. The results from the QUV (figure 3) were somewhat difficult to

interpret but they indicate that a combination of HEPBP and epoxy functionalized soy bean oil gives less discolouration of the wood than the untreated wood.

Future reaction procedure

Due to the temperature dependence of the reaction the procedure will be slightly changed from the initial experiment. The temperature needs to be increased and can in this case be achieved by either changing the solvent or to pressurize the system. First alternative solvents are tested with higher boiling points. Another alternative is to put the system under pressure in a stainless steel reactor which will increase the boiling point of the solvent. A benefit with this system is that acetone can still be used which facilitates evaporation of the solvent. Another interesting aspect is the use of other types of UVA besides HEPBP, which could turn out to be even more successful. It could also be of interest to study other types of catalysts besides DMAP. An advantage with DMAP however is that it does not discolour the wood as has been the case in previous experiments (Westin 2002).

CONCLUSIONS

Pre-treatment of wood with HEPBP as a UVA in combination with an epoxy functionalized soy bean oil show promising results. The FTIR and accelerated weathering tests indicate that the UVA has reacted with the wood and that the oil affects the surface properties of the wood. The temperature is, however, of great importance for the reaction and to get confirmation of the initial results another trial has been started where the temperature is increased.

ACKNOWLEDGEMENTS

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Comparison of Wood Moisture Content in Coated Panels of Selected Types of Modified Wood during Natural Weathering

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Keywords: Modified wood, continuous moisture content measurement, wood coatings, natural weathering

ABSTRACT

Wood moisture content of coated thermally modified, Cr-free impregnated, and furfurylated Scots pine panels as well as coated acetylated Radiata pine panels in comparison to unmodified Scots pine panels during 18 month natural weathering in Vienna was recorded by changes in panel mass and electric resistance. Calibration curves to calculate wood moisture content via electric resistance of thermally modified wood and furfurylated wood were generated. Lab tests on the liquid water uptake were carried out. Both, thermally modified wood and furfurylated wood, coated and uncoated, showed the lowest liquid water uptake, but solely the wood moisture content during natural weathering of furfurylated wood was different to all others, the immediate increase of wood moisture content caused by rain was ten times lower and also the seasonal changes between summer and winter were only half of thermally modified, acetylated and Cr-free impregnated wood. The differences between the other modification methods were smaller. Unmodified coated wood did not show the highest variations, the Cr-free impregnated wood revealed the highest variation in wood moisture content. The results provide evidence on moisture conditions in coated and uncoated modified wood in exterior applications.

INTRODUCTION

The wood moisture content measured by change of panel mass and by electric resistance of unmodified and panels with different modifications, coated and uncoated, during natural weathering according to EN 927-3 as well as simultaneously measured weather data should give evidence on the influence of modification and coating on the change of wood moisture content and enable to analyse the influence of climatic conditions on the change of wood moisture content. The liquid water uptake values according to EN 927-5 should be compared to the change of moisture content during natural weathering.

MATERIAL AND METHODS

Natural weathering trials were carried out with a selection of different types of modified wood. Uncoated and coated unmodified Scots pine sapwood was used as reference. Uncoated panels and panels coated with a semi-transparent 50 µm dry film stain were used to compare different wood modification systems.

Substrates and coating

For *unmodified panels* (UNM) industrially pre-dried Scots pine sapwood (*Pinus sylvestris*) was used. The wood was straight grained, free from defects and the orientation of the growth rings to the face was 5° to 45°. Boards of Scots pine sapwood (*Pinus sylvestris*) were *thermally modified* (thermo) with a maximum temperature of 212°C for a duration of one hour, the ring orientation of the panels was more flat than required in EN 927-3. For *Acetylated* (acetylated) wood a commercial product made from *Pinus radiata* was used. According to information provided by the producer, the acetyl content determined by HPLC and FTIR analyses was above 20%. Panels of Scots pine sapwood (*Pinus sylvestris*) were vacuum/pressure impregnated with a *chromium-free* (Cr-free) wood preservative salt. The concentrated product was diluted in water to a concentration of 3%. The impregnation resulted in a wood preservative uptake of 18.5 kg/m³ (± 1.8 kg/m³). Scots pine sapwood (*Pinus sylvestris*) from south eastern Norway was used for *Furfurylated wood* (furfurylated). Selected panels were modified in a commercial furfurylation process. The average weight percent gain (WPG) after treatment was 97%. Unfortunately, gradients of the furfurylation treatment were detected over the cross sections of several of the samples when they were cut. It was decided to use the samples because in the weathering trials the cross sections were sealed, reducing the effect of the gradient. A semi-transparent *coating system* (C) based on a waterborne acrylic dispersion was used to coat the panels of unmodified and modified wood in two layers by spraying with a target dry film thickness of 50 μ m. As primer a water based alkyd emulsion including dichlofluanide as fungicide was applied by dipping. The end grains of all panels were sealed according to EN 927-3 with 2K-epoxid resin, additionally the backsides the panels for electric resistance measurement were sealed.

Natural weathering

Natural weathering exposure was carried out in Vienna, Austria for 18 months (Nov08 – May10) according to EN 927-3. One panel with artificial hail defects and three without defects for each variation were mounted south oriented in racks inclined 45°.

Moisture content measurement

The panel mass (PM) was measured on the three panels without defects for each system with a calibrated scale (0,01 g) before starting the exposure and during exposure weekly. To this all panels were demounted from the racks, immediately brought into the lab and weighted. The *electric resistance* (EL) was measured on panels with artificial hail defects in the coated surface with isolated pins driven from the back sides of the panels 3 mm beneath the top surface as well as the temperature of wood every half an hour with a Brookhuiss MCM data logger. *Weathering data* was recorded simultaneously with an “Almemo Meteo-Mulitgeber FMA510”. To calculate the wood moisture content for electric resistance method for unmodified Scots pine the software AB-MCM-DEMO vs 1.10 of Brookhuis Micro Electronics BV, curve 210 for *Pinus sylvestris* was used. To calculate the wood moisture content for thermally modified and furfurylated wood with input data of electric resistance and temperature a function generated by University of Göttingen was used, that covered a range of 100 K Ω to 140 M Ω electric resistance. The function was generated from correlation based on measurements with a “Materialfox and Mulitsensor” of Scantronik Mugrauer GmbH, Germany.

RESULTS AND DISCUSSION

Furfurylated Scots pine showed the lowest liquid water uptake (Figure 1) and the lowest variation of wood moisture content during natural weathering (Table 1 and Figure 2). Uncoated acetylated Radiata pine and Cr-free impregnated Scots pine showed higher liquid water uptake than unmodified Scots pine (Figure 1), and the highest variation of wood moisture content during natural weathering (Table 1 and Figure 2). Thermally treated Scots pine showed a low liquid water uptake (Figure 1), as low as furfurylated Scots pine, uncoated only one third of unmodified Scots pine, but during natural weathering the variation in wood moisture content was significantly higher than of unmodified Scots pine and especially of furfurylated Scots pine, which stands in opposite of the expectations.

The electric moisture (EL) content of furfurylated wood (Table 1) showed significantly higher values than with panel mass method (PM), the coating showed no influence, mainly caused by coating cracks and moisture traps and that only panels of PM-method could release moisture over the backside (panels for EL-method were sealed on backside). The coated thermally modified wood showed a higher moisture content level with higher short time variation than coated unmodified wood and quite similar curves in PM-method and EL-method except during heavy rain events where panel mass values were higher (Figure 2). A coating had again a small influence only in the first winter period and afterwards no significant influence was observed because of cracks in coating and substrate from the beginning of exposure (immediate increase in EL-method after start of exposure). Uncoated unmodified Scots pine showed in both methods (EL and PM) the highest wood moisture content level with the highest variation (Figure 2 and Table 1). With both methods (EL and PM) the differences between coated and uncoated unmodified Scots pine could be detected.

Table 1: Weather conditions and wood moisture content (mean \pm standard deviation)

Sample	1 st winter	1 st summer	2 nd winter	2 nd spring	18 months
Time window	Dec08- Feb09	May09- Sep09	Dec09- Feb10	Mar10- May10	Nov08- May10
Weather data					
temperature [°C]	1.2 \pm 3.93	19.9 \pm 4.78	0.7 \pm 4.65	10.4 \pm 6	9.7 \pm 8.95
relative humidity [%]	80.7 \pm 12.51	62.6 \pm 16.1	77.5 \pm 11.78	62.5 \pm 16.33	69.6 \pm 16.98
daily precipitation [mm]	0.7 \pm 1.85	3.5 \pm 8.51	0.5 \pm 1.38	2.5 \pm 6.24	1.9 \pm 5.8
Wood moisture content according to electric resistance (EL) [%]					
EL_U_UNM	25.4 \pm 4.27	18 \pm 6.48	24.6 \pm 2.83	22.9 \pm 6.44	21.9 \pm 6.39
EL_U_thermo	20.8 \pm 3.56	17.8 \pm 3.75	19.5 \pm 3.13	19.8 \pm 2.54	19.7 \pm 3.48
EL_U_furfurylated	23 \pm 0.95	16.9 \pm 3.78	21.5 \pm 1	18.3 \pm 3.3	19.8 \pm 3.6
EL_C_UNM	16.4 \pm 1.12	10 \pm 0.73	14.9 \pm 2.45	14 \pm 4.24	13.1 \pm 3.31
EL_C_thermo	19.1 \pm 2.81	16.8 \pm 3.45	19.1 \pm 3.39	18.3 \pm 2.97	18.6 \pm 3.14
EL_C_furfurylated	22.6 \pm 1.03	17.2 \pm 3.64	22.1 \pm 0.91	19.4 \pm 2.7	20.2 \pm 3.39
Wood moisture content according to change of panel mass (PM) [%]					
PM_U_UNM	28.5 \pm 5.03	15.9 \pm 6.34	28.1 \pm 6.75	23.9 \pm 13.58	22.3 \pm 9.34
PM_C_UNM	20.7 \pm 0.77	12 \pm 1.92	18.4 \pm 0.95	14.5 \pm 2.13	15.6 \pm 3.77
PM_C_thermo	23 \pm 2.76	16.6 \pm 3.93	21.3 \pm 1.01	19.2 \pm 3.71	19.4 \pm 4.18
PM_C_furfurylated	15.5 \pm 0.85	11.3 \pm 0.65	14.3 \pm 0.67	13 \pm 0.76	13.2 \pm 1.84
PM_C_acetylated	19.2 \pm 2.95	15.1 \pm 4.66	19 \pm 1.41	16.9 \pm 4.86	17 \pm 4.15
PM_C_Cr-free	21.3 \pm 1.52	12.7 \pm 4.94	20.7 \pm 2.47	16.3 \pm 5.52	16.6 \pm 5.32

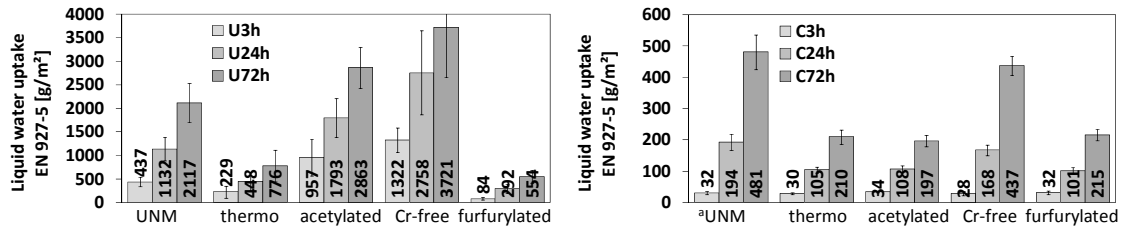


Figure 1: Liquid water uptake of uncoated (U) (left) and coated (C) (right) unmodified (UNM) and modified panels after 3h, 24h, and 72h water storage according to EN 927-5 (mean with standard deviation, n=6); ^acoated UNM: Spruce

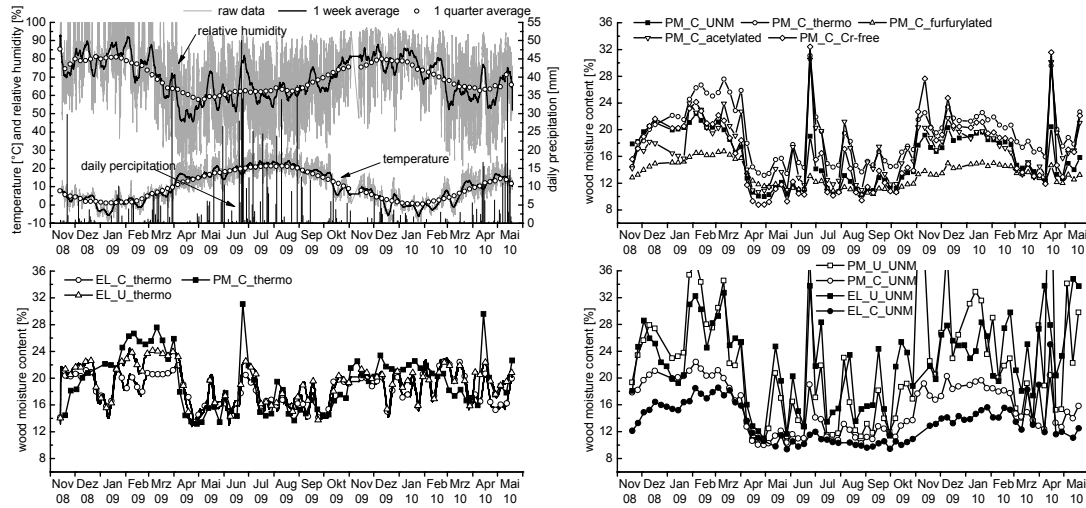


Figure 2: Weather data (top left); wood moisture content of coated panels (PM-method) (top right); wood moisture content PM-method compared to EL-method of coated (C) and uncoated (U) panels (weekly average) (bottom left: thermally modified Scots pine; bottom right: unmodified Scots pine).

CONCLUSIONS

Uncoated thermo Scots pine and furfurylated Scots pine showed a lower wood moisture content level with lower variation than unmodified Scots pine. A significant influence of a coating on wood moisture content could be measured on unmodified wood as long as the coating fulfils its moisture protection function. This influence could not be measured at thermally modified wood and furfurylated wood because of cracks in the coatings and moisture traps from the beginning of exposure. When coated, only furfurylated Scots pine showed a significantly lower wood moisture content level and lower seasonal and short time variation than unmodified Scots pine, all other wood modification methods as acetylated Radiata pine, thermally modified Scots pine and Cr-free impregnated Scots pine, showed a similar or higher wood moisture content variation than coated unmodified Scots pine, which fits with the liquid water uptake values according to EN 927-5, with exception of thermally treated wood.

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Plasma Modification of Wood Surfaces to Improve the Performance of Clear Coatings

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Keywords: Black spruce, clear coatings, penetration, plasma

ABSTRACT

Clear coatings on wood transmit solar radiation which can degrade wood beneath the coating. The coatings themselves do not penetrate into wood beyond the depth that is affected by solar radiation and hence photodegradation of wood beneath clear coatings causes significant loss of coating adhesion and performance. The performance of clear coatings might be improved if clear coatings could penetrate more deeply into wood and bond with sub-surface layers that are less affected by light. The penetration of adhesives into wood can be increased by treating wood with glow-discharge plasma and we hypothesise that similar plasma treatments will increase the penetration of clear coatings into wood. To test this hypothesis, black spruce wood was treated with glow-discharge plasma and the penetration of oil and water-borne clear coats into the wood was measured. Prolonged plasma treatments increased the penetration of both oil and water-borne coatings into sub-surface wood layers. Research is in progress to examine whether these increases in coating penetration will improve the adhesion and performance of clear coatings on wood exposed to artificial accelerated weathering.

INTRODUCTION

Clear coatings perform badly on timber during exterior exposure due to photodegradation of wood beneath the coating and loss of interfacial adhesion between the coating and wood. UV radiation and the photoactive component of the visible spectrum penetrate and degrade wood to a maximum depth of 500 μm . Normally coatings do not penetrate beyond this depth and hence their performance is badly affected by surface photodegradation of wood. The performance of such coatings might be increased, however, if they could penetrate into wood and bond with the subsurface layers that are less affected by light. The penetration of coatings into wood can be increased by treatments that increase the permeability of wood. For example, Singh et al. (1998) showed that storing wood in ponds, where wood is colonized by bacteria that destroy pit membranes, significantly increased the penetration of coatings into radiata pine wood. Pit membranes in wood can also be degraded by plasma (Jamali and Evans 2010), and the permeability of wood can be increased by plasma treatments (Chen and Zavarin 1990). Therefore, it is possible that plasma pre-treatment of wood might increase the penetration of clear finishes applied to wood and this might have beneficial effects on the performance of the coatings. The aim of this study was to examine the effect of plasma treatments on the penetration of two different types of clear coatings into wood.

EXPERIMENTAL

Four air-dry, planed, quarter-sawn black spruce (*Picea mariana*) boards measuring 60 mm (width) x 25 mm (thickness) and 450-500 mm (length) were conditioned at $20 \pm 1^\circ\text{C}$ and $65 \pm 5\%$ relative humidity for 15 days. One panel measuring 18 x 6 x 450 mm was cut from each board and each panel was cross-cut into two samples, which were allocated at random to the two different types of clear coatings. Five specimens measuring 18 x 6 x 20 mm were cut from each sample and allocated to the different plasma treatments including the untreated control. Samples were exposed to glow discharge plasma for 0.5, 3, 10 or 20 minutes using the plasma reactor and reaction conditions described previously (Jamali and Evans 2010). Samples subjected to a vacuum (19.998 Pa) in the plasma reactor acted as a control. Two different types of clear coatings were purchased commercially: (1) Solvent-based urethane (Minwax Helmsman spar urethane); (2) Water-based urethane (Varathane diamond spar urethane). The different coatings were applied to the specimens using a calibrated micropipette and then brushed across the surface using a fine brush that was loaded with coating. The thicknesses of the coatings were approximately 125 μm . The coated surfaces were air dried at $20 \pm 1^\circ\text{C}$ and $65 \pm 5\%$ r.h. for 10 days, lightly sanded with abrasive paper and a second layer of finish was applied to the specimens, as above. Transverse sections ($\sim 30 \mu\text{m}$ thick) were cut from the central region of each coated and treated specimen. Each section contained at least one complete growth ring. Sections were stained with 0.1% Sudan IV (in 80% ethanol) to make the coating easier to see. The sections were mounted in distilled water on glass slides and examined with a Zeiss microscope equipped with an Olympus DP71 digital camera. One representative digital (TIFF) photograph of a complete growth ring was obtained for each specimen. Digital photographs were loaded into the image analysis software (Definiens eCognition), and coated and uncoated areas measuring 5 x 5 pixels on the images were identified. These classified images were loaded into AutoCad together with the original image. A line was drawn on the image at the interface between the wood and coating, and the centre of each cell was identified using a point. Each image was sub-divided incrementally from the wood surface into depth zones that were each 25 μm thick (0-25 μm , 25-50 μm and so on) based on the minimum Euclidean distance from each cell to the closest point at the wood/coating interface. The amount of coating within each zone was quantified as the ratio of coated pixel elements to the total number of classified elements. Analysis of variance was used to examine the effect of coating and plasma treatment on the amount of coating in each of the first three 25 μm layers of wood.

RESULTS AND DISCUSSION

The solvent-borne clear coating penetrated untreated black spruce wood to a depth of $\sim 300 \mu\text{m}$ (Fig. 1a-b). The penetration of the water-borne coating into untreated black spruce wood was approximately half that of the solvent-borne coating, although occasionally cells that contained water-borne coating could be found deeper in the wood (Fig. 1c). Both the solvent and water-borne coatings filled approximately 55 percent of the void space at depths of up to 25 μm in untreated wood (Fig. 1a-c). Thereafter there was a drop in the percentage of void space filled with coating, which was more pronounced for wood coated with the water-borne coating (compare Fig. 1a with Fig. 1c).

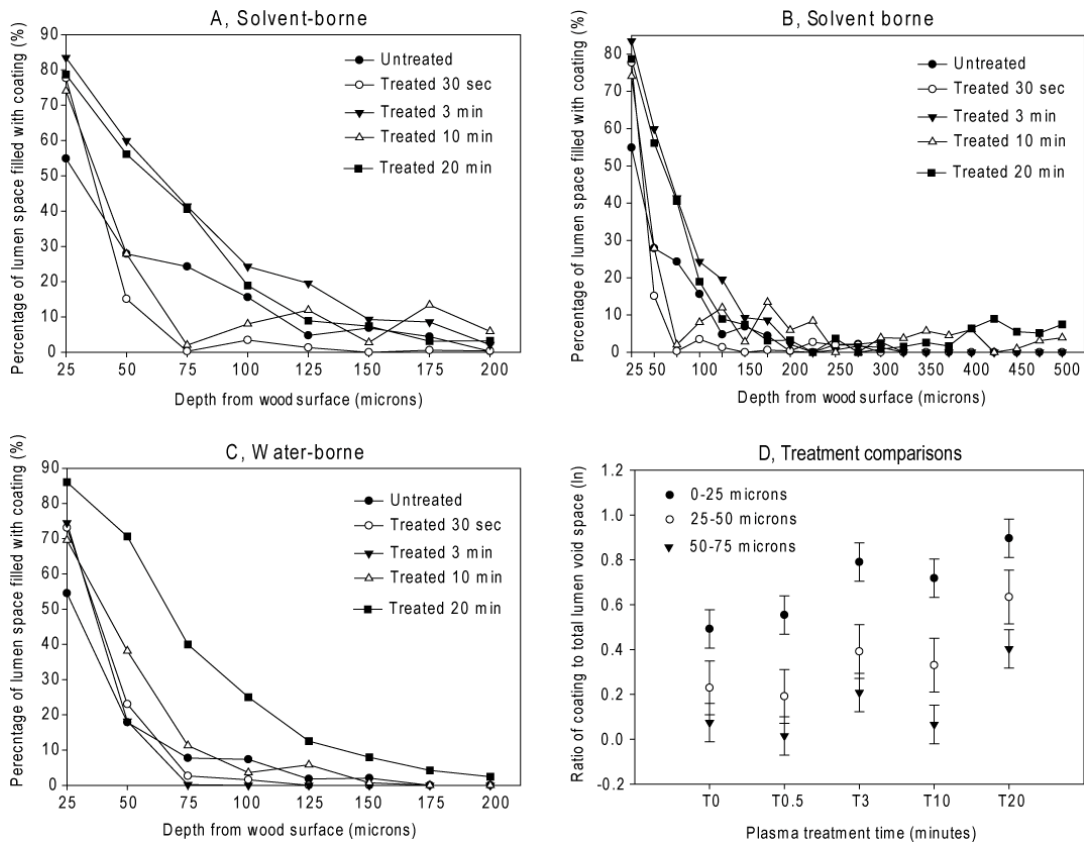


Figure 1: Effects of plasma treatments on the penetration of clear-coatings into black spruce wood.

Prolonged plasma treatment for 10 and 20 minutes increased the penetration of the solvent-borne coating into wood to 500 μm , compared to 300 μm in the untreated control although at a depth of 500 μm less than 10 percent of cell lumens were occupied by coating material (Fig. 1a,b). Prolonged plasma treatment for 20 minutes also increased the penetration of the water-borne coating to 200 μm compared to 150 μm in the untreated control (Fig. 1c). Prolonged plasma treatment for 20 minutes also significantly increased the percentage of void space occupied by coating material. Figure 1d compares the effects of the different plasma treatments on the percentage of void space occupied by coating material at depths of 0 to 25 μm , 25 to 50 μm and 50 to 75 μm . The results are the averages for both the solvent-borne and water-borne coatings because analysis of variance revealed no significant ($p > 0.05$) interaction of coating type and treatment on the percentage of void space occupied by coating material. Plasma treatment for 3, 10 and 20 minutes significantly ($p < 0.05$) increased the percentage of void space occupied by coating material in the zone immediately below the wood surface from 0 to 25 μm . However, at depths of 25 to 50 μm and 50 to 75 μm only prolonged plasma treatment for 20 minutes significantly ($p < 0.05$) increased the percentage of void space occupied by coating material. The effects of prolonged plasma treatment on coating penetration can be easily seen in Figure 2. Figs 2A and 2C show the penetration of solvent-borne and water-borne coatings into untreated black spruce wood, respectively. Figs 2B and 2D show the effects of 20 min plasma treatment on the penetration of solvent-borne and water-borne coatings into black spruce wood, respectively. These photographs of the coating/wood interface clearly demonstrate that prolonged plasma treatment increased the penetration of clear coatings into black spruce wood.

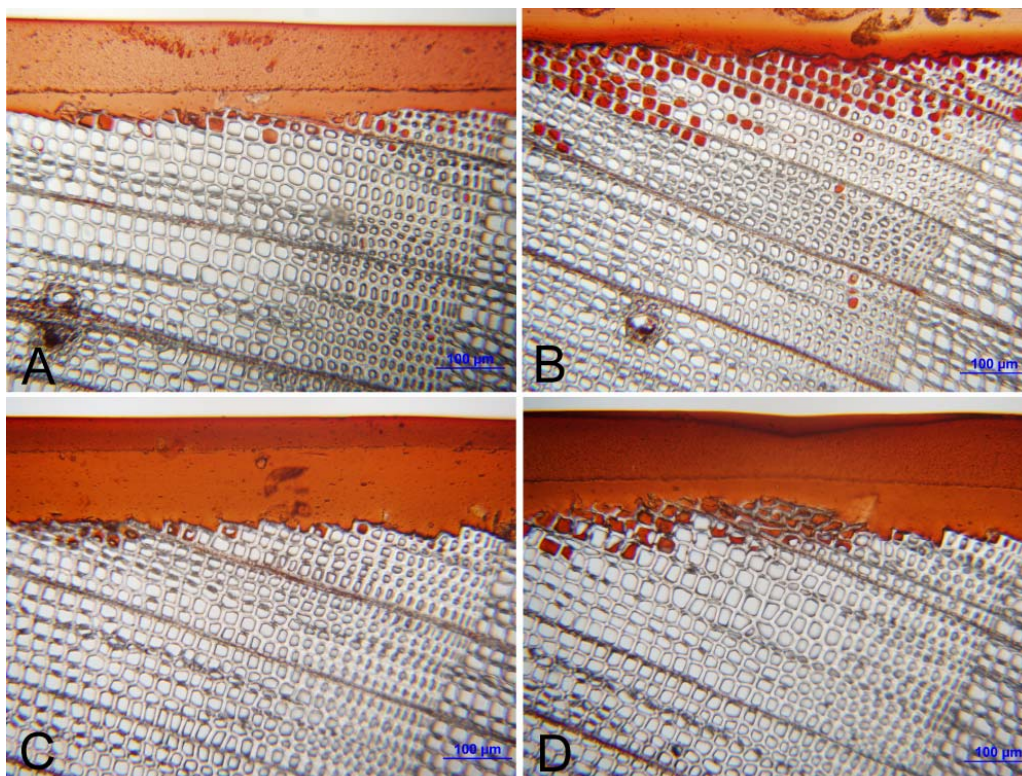


Figure 2: Effects of prolonged plasma treatment on the penetration of clear coatings into black spruce.

Research is in progress to examine whether increases in coating penetration resulting from prolonged plasma treatment can improve the performance of clear coatings exposed to artificial accelerated weathering.

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**Session Six:
Environmental Issues, Resins,
Waxes and Others**

Carbon Footprint Assessment for Acetylated Wood Applications

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Keywords: acetylated wood, greenhouse gas emissions, carbon footprint, environmental assessment, applications, annual yield, life cycle analysis

ABSTRACT

In a carbon footprint assessment, the greenhouse gas emissions [GHG] during the life cycle of a product or material can be quantified. Wood acetylation opens up a range of innovative applications in which energy intensive non-renewable materials such as metals, plastics and concrete may be substituted. To better understand the difference in emissions of Accoya[®], an acetylated wood product, and relevant alternative materials (steel, concrete, plastics, and hardwood), this study presents the results of a comparative carbon footprint assessment for the application of a pedestrian reference bridge and a window frame. The assessment was based on a “cradle to grave” scenario and therefore includes aspects related to the use-phase such as material use, durability, carbon sequestration and maintenance. If life span considerations are included, acetylated wood has a considerably lower carbon footprint than non-renewable and unsustainably harvested hardwood, and is competitive in terms of carbon footprint with sustainably sourced hardwood. Finally, this paper discusses the difference between carbon footprint and Life Cycle Assessment (LCA) as environmental impact assessment tools, and the affects of exclusion of the renewability aspect in terms of annual yield of wood products in these methodologies.

INTRODUCTION

In a carbon footprint assessment, the GHG emissions during the life cycle of a product or material can be measured, and compared to alternative products. Through wood modification, the carbon sequestration effect of wood may be lengthened by increasing the durability of wood. Most modification technologies result in the emission of GHG's. Thus it is important to better understand to what extent the increased durability of modified wood outweighs the increased emissions caused by the modification process and in comparison with alternative non-renewable materials.

METHODOLOGY

Carbon Footprint Methodology

In a GHG emissions assessment, also known as a carbon footprint assessment, the impact human activities, products and materials have on the emission of green house gases can be quantified. Although not as comprehensive as the Life Cycle Assessment (LCA) methodology, as defined in the ISO 14040/44 series (ISO 2006), which besides the Global Warming Potential (GWP), also includes environmental effects such as toxicity, acidification and eutrophication, a carbon footprint assessment is an excellent tool to assess a product or service's environmental impact.

A carbon footprint assessment was executed for Accoya[®] wood (Muss and Purse 2009) in line with the World Business Council for Sustainable Development and World Resources Institute's (WBCSD/WRI) Greenhouse Gas Reporting Protocol best practice guidelines (Bhatia and Ranganathan 2004), which encompasses the six GHG's covered by the Kyoto Protocol: carbon dioxide (CO₂), methane (CH₄), nitrous oxide (N₂O), hydrofluorocarbons (HFCs), perfluorocarbons (PFCs), and sulphur hexafluoride (SF₆). As these gases all have a different impact on Global Warming Potential, thus they are translated to a single unit: carbon dioxide equivalent (CO₂eq), which is the most widely accepted method of reporting all Kyoto GHG's. The carbon footprint assessment of Accoya[®] wood by Muss and Purse (2009) was executed based on a "cradle-to-gate" scenario as outlined below. As a result, the cradle till gate assessment still lacked the in-use phase considerations in an actual application ("cradle-to-grave"), thus an expanded approach is also included in this paper, to provide a more holistic comparison with other materials.

Cradle till Gate Data (Production Phase)

The cradle till gate carbon footprint assessment by Muss and Purse (2009) included the emissions related to the following aspects of the Accoya[®] production process:

- The embodied energy of the primary materials (i.e. the total energy that was used to manufacture the material);
- Fuel consumed for timber harvesting and transportation to the processing facility;
- The energy consumed during sawmill operations;
- The energy consumed during timber acetylation process;
- Waste produced during the manufacturing process.

The main input resources to produce acetylated wood are timber and acetic anhydride. We have adopted a realistic and conservative scenario for timber and acetic anhydride sourcing. We have assumed Radiata Pine from New Zealand as input timber. Acetic anhydride is generally produced through either methyl acetate carbonylation, or the more energy intensive ketene route. A "production mix" was assumed for acetic anhydride which is related to the weighted average of the emissions of the two routes based on worldwide production capacity for both technologies. During the acetylation process, acetic acid is produced as co-product. This acetic acid is sold into a wide range of industries and therefore replaces merchant acetic acid on the market. As such the allocated GHG emissions of acetic acid are deducted from the emissions relating to the acetylation process, which is in line with PAS 2050 requirements (BSI group 2008).

In Figure 1, the carbon footprint factors are presented for various building materials, including Accoya[®], based on a cradle till gate scenario and based on cubic meters of building material produced.

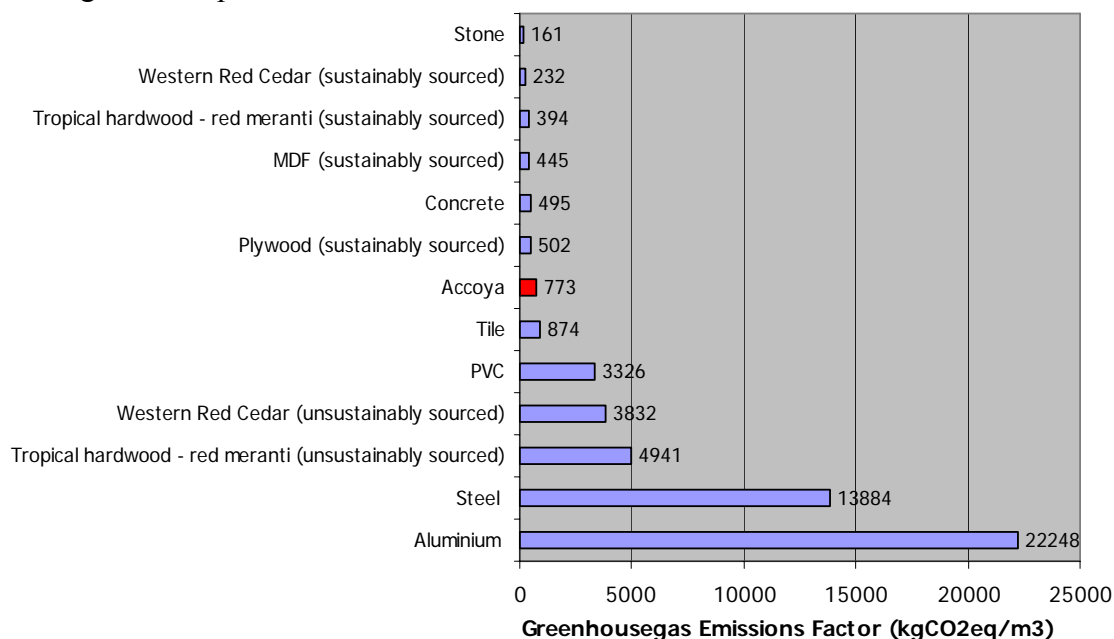


Figure 1: Greenhouse gas emissions per cubic meter of building material in kg CO₂ equivalent (Muss and Purse 2009).

Cradle till Grave Data (Including Use Phase)

It is important to understand that the carbon footprint per cubic meter provides limited information for a realistic comparison with other materials since additional use-phase related aspects of the various material alternatives such as material use, durability, maintenance and carbon sequestration are not yet included. Therefore, for a fair comparison, the carbon footprint results per cubic meter need to be translated into actual applications in which these additional aspects are included.

For this assessment, applications were chosen in which Accoya[®] and other relevant wood alternatives for outdoor use could be compared with non-renewable and typical materials for a window frame and the bearing structure of a pedestrian bridge. For a fair comparison, in these applications, all alternatives need to have the same functional unit/requirement (e.g. for the pedestrian bridge: equal load requirements).

The carbon sequestration effect of wood is included in this cradle till grave carbon footprint assessment by adopting the PAS 2050 methodology (BSI group 2008) developed by the UK government for environmental assessments, through which the CO₂ locked into the wood can be included as a negative CO₂eq value. A higher negative CO₂eq value is allocated, if the life span of the wood in-use is longer, which is beneficial for Accoya[®] due to calculated life spans of 50 years or greater in most applications.

Note that “sustainably sourced wood” in this paper relates to a relatively consistent biomass at the forestry level, in which the carbon stored in the standing volume remains stable. In this paper “unsustainably sourced wood” relates to clear cutting practices.

Due to the complexity and lack of availability of reliable data, end-of-life aspects such as the possible incineration of wood products for energy production, which could provide marginal additional carbon saving advantages for wood products, if fossil fuels are substituted, are not included in this assessment.

Window Frame

The functional unit chosen for the window frame was adopted from Richter et al. (1996) and is expressed as “one window frame with the outer dimensions of 1650 mm x 1300 mm with a total surface of 4,38 m² (interior and exterior)”. Relevant alternatives for this application were tropical hardwood (red meranti), both sustainably and unsustainably sourced, aluminium and PVC. Lifespan assumptions were made by a thematic expert, Mr Jan de Jonge of TNO Bouw in the Netherlands. Lifespans for the window frame alternatives were assumed to be solely determined by the durability of the frame, and are based on a typical Dutch window frame, well executed and maintained.

While aluminium and PVC do not require coating maintenance throughout the lifespan, wood alternatives, including Accoya[®], do. The high dimensional stability and other benefits of Accoya[®] mean that it requires less frequent coating maintenance (Bongers and Creemers 2005). Coating frequency and volume for this assessment was determined by maintenance specialist Jan Huizer of Weijman Real Estate Maintenance who produces and maintain a complete window frame system based on Accoya[®], called Endura, presented at ECWM 4 (Huizer, 2009). A concept III window frame system (totally prefabrication at the joinery factory) with a specified amount of white Alkyd paint was assumed. Weijman Real Estate Maintenance found from their own experience that the primer layer for Accoya[®], even after a longer maintenance interval, does not need to be completely reinstalled (only refined) in contrast with other wood species including Meranti, explaining the thinner coating layer during maintenance.

In Tables 1 and 2 all the assumptions made for the comparative carbon footprint assessment of the window frame are provided.

Table 1: Material use, lifespan and carbon sequestration assumptions made for the carbon footprint assessment of a window frame

Material	Amount of material per frame	Emissions factor per frame	Lifespan [yrs]	Carbon sequestration benefit [kgCO₂eq/m³]
Accoya [®]	0.0838 m ³	773 kgCO ₂ eq/m ³	50	- 413
Tropical hardwood - red meranti (sustainably sourced)	0.0838 m ³	394 kgCO ₂ eq/m ³	35	- 411
Tropical hardwood – red meranti (unsustainably sourced)	0.0838 m ³	494 kgCO ₂ eq/m ³	35	- 411
Aluminium	39.65 kg	8.24 kgCO ₂ eq/kg	50	N/A
PVC - steel window frame	<i>PVC</i> : 25.6 kg <i>Steel</i> : 16.1 kg	2.41 kgCO ₂ eq/kg 1.78 kgCO ₂ eq/kg	35	N/A

Table 2: Coating assumptions for wood alternatives made for the carbon footprint assessment of a window frame

Material	Amount of coating in wet conditions per frame over lifespan	Emissions factor [kgCO ₂ eq/kg]
Accoya®	3,56 kg over 50 years	2.786
Tropical hardwood (red meranti)	5,55 kg over 35 years	2.786

Pedestrian Bridge

The principal structural engineer of the Accoya® based Sneek bridge, Mr. Emil Lünig, designed the bearing structure of a reference pedestrian bridge, which would facilitate a just comparison for various material alternatives. The pedestrian bridge had to comply with all relevant Dutch building legislation for such a bridge. Figure 2 shows the schematic plan of the load bearing structure.

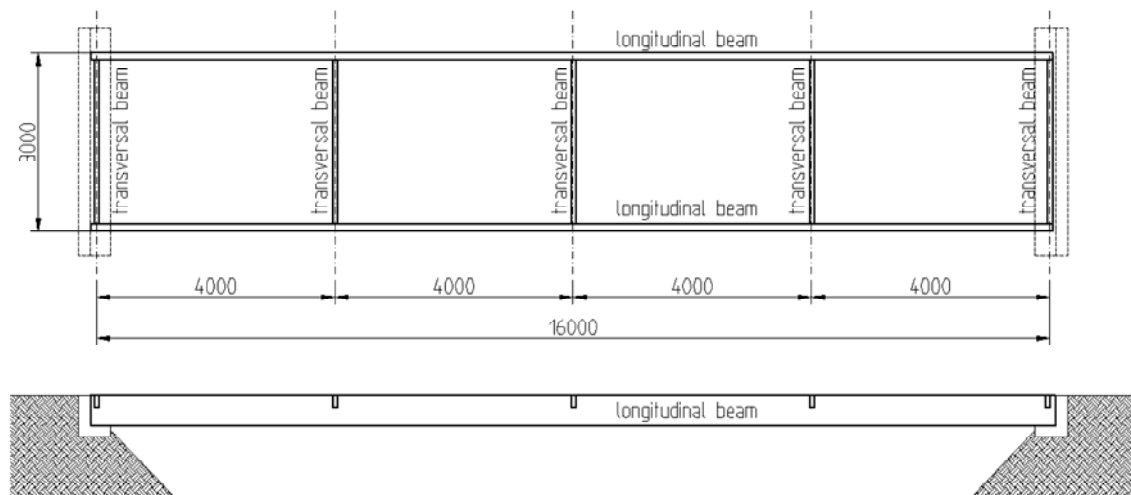


Figure 2: Constructional plan of the reference pedestrian bridge, above-view (top) and the side-view (bottom) (Lünig and Tran 2009)

Table 3: Assumptions made for the carbon footprint assessment of a pedestrian bridge

Material	Amount of material per bridge	Emissions factor	Lifespan [yrs]	Carbon sequestration benefit [kgCO ₂ eq / m ³]
Accoya® wood	Accoya®: 6,41 m ³ Glue (PU): 0,096 m ³	773 kgCO ₂ eq/m ³ 4.694 kgCO ₂ eq/kg	80	- 660
Tropical hardwood – Azobé (sustainably sourced)	Azobé: 5,94 m ³ Steel: 297 kg	304 kgCO ₂ eq/m ³ 1.78 kgCO ₂ eq/kg	50	- 972
Tropical hardwood – Azobé (unsustainably sourced)	Azobé: 5,94 m ³ Steel: 297 kg	4851 kgCO ₂ eq/m ³ 1.78 kgCO ₂ eq/kg	50	- 972
Reinforced concrete	Concrete: 11,43m ³ (density 2400 kg / m ³) Steel: 803 kg	516 kgCO ₂ eq/m ³ 1.78 kgCO ₂ eq/kg	90	N/A
Steel (hot dip galvanized)	4437 kg	1.78 kgCO ₂ eq/kg	50	N/A

Table 3 summarizes the material use based on structural calculations and lifespan considerations. No coating maintenance has been assumed for the pedestrian bridge case.

RESULTS

The combined assumptions for these two applications provide the annual emissions per application and a just comparison in terms of carbon footprint. In Figures 3 and 4, the annual emissions per window frame and pedestrian bridge are provided.

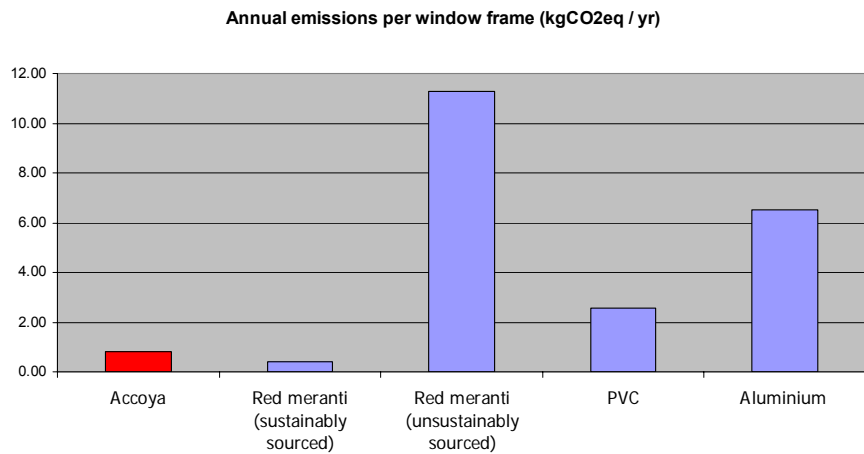


Figure 3: Annual emissions per window frame

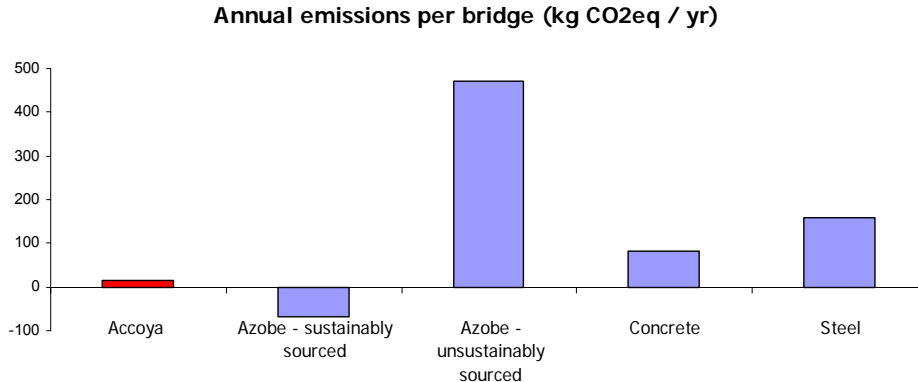


Figure 4: Annual emissions per pedestrian bridge

The graphs show that in terms of annual carbon footprint, Accoya[®], for both applications, performs significantly better than metals (steel, aluminium), plastics (PVC), unsustainably sourced timber and concrete, while performing slightly worse than sustainably sourced timber. From Figure 4, it becomes clear that sustainably sourced wood, through the carbon sequestration effect modelled through the PAS 2050 guidelines, in some cases may even have a negative carbon footprint. On the other hand, when unsustainably sourced, the annual emissions increase dramatically.

CONCLUSIONS & DISCUSSION

In this study the results of a comparative carbon footprint assessment for the application of a pedestrian bridge and a window frame are presented for Accoya[®] wood with relevant material alternatives. While sustainably sourced timber was slightly lower, and in some cases even had a negative CO₂ carbon footprint, Accoya[®] has a considerably lower carbon footprint than unsustainably sourced timber and materials based on non-renewable resources such as steel, PVC and concrete. Furthermore, modified wood products based on fast growing timbers have other benefits which are not included in a carbon footprint assessment. First, supply of sustainably sourced, certified (tropical) hardwood, is relatively small and importation of illegal hardwoods is still common practice. The Worldbank estimated the annual import of illegally sourced wood in Europe at 20 million cubic meters in 2006. Second, the Mean Annual Increment (MAI) yield of certain renewable materials is not included in the carbon footprint methodology. Thus the selection of wood type should be of great concern to architects and engineers.

Accoya[®] is produced from Radiata pine (*Pinus radiata*). Figure 5 compares the annual yield of various relevant wood species. Radiata Pine has a Mean Annual Increment which is almost five times as high as plantation grown teak. Radiata Pine even outperforms Phyllostachys Pubescens (Moso bamboo), known to grow incredibly fast.

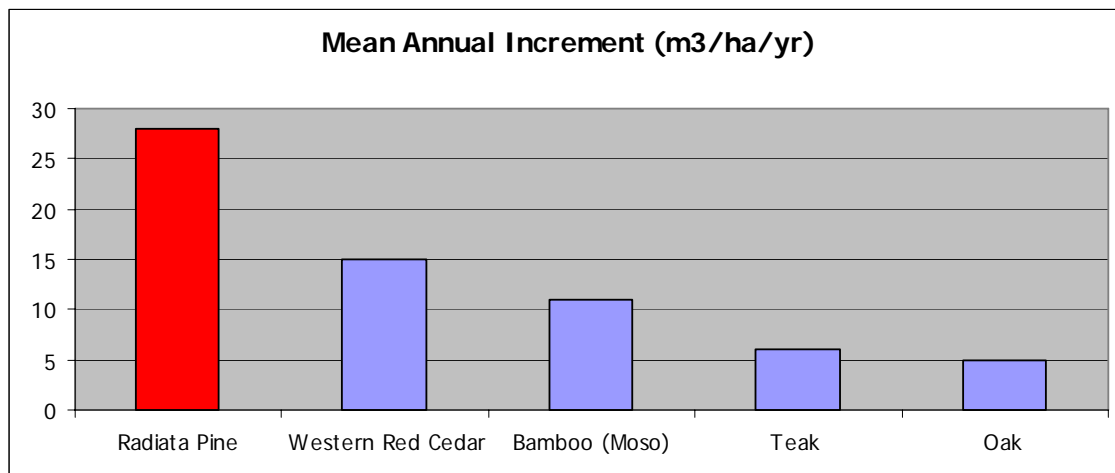


Figure 5: Mean Annual Increment of various renewable materials (Cossalter and Pye-Smith 2003, MAF 2008, Sikkema and Nabuurs 1995, van der Lugt 2008)

Future Developments and Outlook

Cradle till gate carbon footprint assessment provides thorough insight into the carbon intensity for a process. Through GHG analysis company's can refine their production processes to achieve shorter batch times, lower energy consumption and improved renewable energy content. Finally, use of local wood species for Accoya[®] production is underway, which may reduce transport emissions.

ACKNOWLEDGEMENTS

Accoya[®] is a registered trademark owned by Titan Wood Limited, a wholly owned subsidiary of Accsys Technologies PLC.

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Recycling of Modified Wood Products

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Keywords: Recycling, re-use, waste utilisation, wood products

ABSTRACT

Most of the wood waste from building construction and demolition sites ends up to energy production in northern Europe. In southern Europe, most of the waste wood is used in particle and fibreboard production, whereas in central Europe these two end uses more or less compete with each other. Still quite significant proportion of waste ends up to landfill, which is against the goals of EU's waste directives. National laws and EU directives force nations to use wastes more efficiently. This means that an increasing proportion of wastes should be recycled instead of landfilling or burning. Different kinds of modified wood products have become an essential part of normal consumer markets since the 1990's. A common feature to all wood modification methods is that the lifetime of the modified product is intended to be longer than that of unmodified product. To some extent, modified wood products have already effected, and will increasingly effect on the recyclability of timber structures, thus also effecting on the environmental competitiveness of wood products against other materials. Obviously these viewpoints have not been taken into consideration when planning structures consisting of or partly including modified wood. Claddings, for instance, are often made of modified wood nowadays. Walls facing towards south are most severely exposed to UV radiation in European conditions. Therefore, southern walls also most often define the cladding's life span. When the cladding renovation takes place, all walls are likely to be painted or changed instead of the southern wall only. In case of change of cladding, a lot of useful material is recovered from other walls than the southern one, and nowadays treated as waste. If cladding elements that are not only easy to install but also easy to remove would be available, much wood material could be recycled for secondary uses instead of landfill or burning into energy. This paper addresses viewpoints concerning the influence of modified wood on the recyclability of wood products. We summarize relevant matters related to waste management laws and directives, waste wood flows in Europe, and current waste management practices. Based on this review, conclusions are drawn concerning the wood modification industries, and related R&D.

INTRODUCTION

As soon as a product reaches the end of its primary life cycle, it turns either into landfill waste that requires certain waste management (collection, transportation, landfilling) or recovered material that is recycled, re-used or burned into energy. Burning of recovered wood is still not very common. For instance, only 735,000 tons of recovered wood was burned into energy in Finland in 2008 (Statistics Finland 2009). Re-using means that the material or product is used in the same end use purpose for a second time. Recycling means that the material or product is used in a different end use after its primary use. In this article, we use the term "waste" for all materials after their primary use. Thus, "waste" includes both "landfill waste" that ends up to landfill, and "recovered

materials” that are collected for re-use, recycling or energy production. According to Srdjevic *et al.* (2007), recovered wood mainly originates from construction and demolition activities, residential and commercial sectors, furniture and packaging materials. The most important parameters describing recovered wood are mechanical properties, heating value, moisture content and the content of chlorine, ash and heavy metals. Jungmeier *et al.* (2005) estimated the available potential of recovered wood to be approximately 50–100 million dry tons per year. In current societies, the volume of landfill waste is minimised by favouring re-use, recycling or burning into energy. Yet, as much as 45 million tons of landfill waste is produced for example in Finland annually, of which some 25,000 tons is wood based waste (Statistics Finland 2009). The proportion of recycling increases steadily, but we still have a lack of knowledge concerning the possibilities provided by recycling of demolition wastes, for instance. During the past few decades the range of wood products has increased with some new inventions. Some of them have even been commercialised, i.e., the inventions have turned into innovations. One example of the new product groups are wood-based composites, another example, with certain similarities to the composites, are modified wood products. Wood-based composites can easily be recovered (melted) for secondary use, or burned. This paper reviews questions and challenges related to wood product recycling from the viewpoint of modified wood products.

METHODS

The data and results concerning wood product recycling in Finland, Europe and United States is based on an unpublished preliminary study by Pirhonen *et al.* 2010. This paper lists the facts related to waste management and recycling, and, based on inductive reasoning, draws conclusions related to modified wood products. Various statistics databases have been utilised in assessing the waste supplies. Expert interviews were used to ensure that the relevant laws, directives and standards were interpreted correctly.

RESULTS AND DISCUSSION

Laws, directives and standards

A number of national laws, EU directives, as well as standards are associated with production, management, recycling and disposal of various waste flows. Here, we set the focus on general restrictions and future prospects. The basic principle in the European waste management directives is that materials should be primarily recovered for secondary use, and, as a secondary option, they can be utilised as energy. The general idea of the legislation is to prevent waste generation, facilitate its utilisation, and reduce the disadvantages caused by waste management. Materials can be landfilled only if their utilisation is either technically or economically impossible. The European Union has set an objective to develop itself as a recycling society, where waste generation is avoided, and wastes generated are utilised as a resource. The newest waste directive from year 2008 contains an article for re-use and recycling of materials. Among other things, it requires that the member countries have to proceed with necessary actions to recycle materials and products. For instance, Finland is allowed to landfill at most 25% of the biodegrading waste generated in 2016. To fulfil the normative requirements, the industries and R&D should develop products that can be easily recycled. This idea generally favours materials and products that have higher durability than their competitors, i.e., one of the key motivations for wood modification. Green building

certification systems, such as LEED and BREEAM, set requirements for raw materials used in construction or renovation. One of the elements considered when applying for green building certification is the proportion of recycled materials used in buildings.

Recovered wood flows and their current utilisation

Currently, there are two main end uses for recovered solid wood products. One is wood based panel manufacturing (fibreboards, particleboards)(e.g., Maloney 1993, Gann *et al.* 2005), and the other is burning for energy production. In terms of waste management, the most valuable wastes are most efficiently recycled. Paper products can be utilised for instance as insulation materials (Figure 1). A growing proportion of recovered solid wood is chipped for burning in Finland (Figure 2). Table 1 outlines the current principal uses of modified wood products, as well as their property requirements. Here, we analyse the end use groups from two optional viewpoints. Firstly, modified wood products are considered as producers of recovered materials and, secondly, secondary products that could be made of recovered modified wood are outlined. Generally, the larger dimensions the product has, the higher potential it has for recycling or re-use. Products made of small particles, such as fibreboards or particleboards, can possibly be re-used, but have limited possibilities for recycling, i.e., utilisation as different products. Larger products, such as utility poles, have a broad variety of further uses since they can be cross cut to shorter lengths, sawn or chipped basically similarly to ordinary logs. Furniture, decking and cladding materials also show high potential for recycling, since typically the entire structure is changed after a minor damage in limited area. With some preconditions related to the possible chemical treatments applied, modified wood products can be utilised in particleboard or fibreboard production after their primary use. Once recycled into new products, modified wood can provide the panel industries with products showing superior performance. Other way around, traditional products, such as oriented strand boards or other wood-based panels can be modified in order to get their properties improved (e.g., Del Menezzi and Tomaselli 2007). Such products provide a new kind of raw material source after their primary use. Another example are side products originating from production processes of modified wood products. A good example of these is Thermowood® shavings and saw dust that will be used in wood plastic composite manufacture by Lunawood Ltd in Finland. These raw materials provide the composite products with better dimensional stability than ordinary wood does. The same idea could be utilised in wood based panel production, as well. So far, the problem has been the limited availability of recovered modified wood or modified side products such as shavings. This is reasoned by the fact that the majority of the modified products are still in their primary use, and, on the other hand, the quantities of modified side products have been too small for panel manufacture. Obviously the availability of recyclable modified wood can be expected to increase in the near future. At that time there should be other uses considered than burning, since the demolished modified products can constitute a valuable raw material source for new types of wood product industries, or even for pulp and paper industries in small scale. Products' resistance against decay, mold or insects, as well as its durability against moist conditions and weather exposure are necessary features in many of the end use categories of modified wood products (Table 1). Basically all modification methods aim to improve these properties. Therefore, also secondary products made of recovered modified wood will presumably perform better than unmodified products when we consider these property requirements.



Figure 1: Insulation materials made of wood fibres or recovered paper. Photo: Henrik Heräjürvi.



Figure 2: Recovered solid wood is often chipped for burning in the Nordic countries. Its moisture content is low which makes it very desirable material for heat and power production. The same material could easily be utilised in selected wood products, as well. Photo: Henrik Heräjürvi.

Recycling and modified wood products

A common feature to basically all wood modification methods is that they aim to prolong the life span of the products. This can be achieved with (e.g., Belmadur®, Accoya) or without (e.g., Thermowood®) added chemicals. If the life span of modified wood products is longer than unmodified ones, we should also consider the aspect of recycling. Screening and cleaning of chemicals is a major challenge, if such procedure is necessary. We can also think of utilising selected recovered modified wood in products that take the advantage of the chemicals involved in the raw materials.

Table 1: General property requirements of modified wood products by end use category. Explanations: +++ (very important or a precondition); ++ (important); + (at least necessary); – (usually unnecessary).

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	–	–	+	+	++	++	–
Utility poles	+++	–	+++	+	+ ¹⁾	–	–
Other exterior uses ²⁾	+	(+)	++	+	+	+	++
Marine structures	+	+	+++	+	+	+	+

¹⁾ Could be a marketing factor.

²⁾ Such as fences, poles, posts, shelters, etc.

Modified wood products are becoming more common in demanding load bearing structures that are exposed to weather. These include at least bridges and traffic barriers. High durability should also mean high recyclability. For instance, highway traffic barriers have to be replaced after minor damages. This means that a considerable proportion of the replaced material should be in relatively good condition for either re-use in less demanding structures or recycling for other products. Utility poles are traditionally made of pressure impregnated softwoods (e.g., *Pinus sylvestris*, *Pseudotsuga menziesii*) or concrete, making up an interesting product group that is still relatively virgin to modified wood products.

CONCLUSIONS

In terms of wood based waste management, most work is needed with construction and demolition wastes. In Finland, some products have to be recycled based on the so called producer responsibility law. These include, e.g., papers, packing materials, electric devices, batteries, and car tyres. The most efficient recycling systems have been developed for the most valuable materials that are, in many cases, actually recycled much more efficiently than the producer responsibility law requires. One way to improve the effectiveness of recycling activity is to broaden the variety of products belonging to the producers responsibility. Building construction systems are experiencing dramatic changes since the environmental performance issues are getting more and more attention among the consumers. In addition, houses are built to fulfil tightening energy efficiency requirements especially in North and Central Europe. At its easiest, the energy efficiency is improved by increasing the thickness of the insulation material. However, such solution sets obvious demands to the structures, influencing, e.g., their dimensional stability, susceptibility to mould and decay, stiffness and strength. All these requirements being more or less resolved by the use of modified

wood products. The big challenges lie in the technical solutions that are still underdeveloped, as well as the cost competitiveness of modified wood products against pressure impregnated wood or metal, plastic and concrete structures. Considerable investments in R&D are necessary to be able to defeat these challenges. Among other things, the green building certification systems call for recycled materials. During the past few years, more and more people and nations have understood that sustainable economical growth is not anymore only dependent on funding or markets. Instead, the true limiting factors are inadequate availability of natural resources and ecological capacity of the Earth. However, industrial and economic policies are still widely based on traditional frameworks: quarterly planning, short-term profits, aiming at ever increasing sales, etc. We should gradually set the focus on savings, energy efficiency, and durable products with high recyclability. Modified wood products can and will be a crucial part of this development. This idea of entrepreneurship, research and development based on sustainable solutions, which we call here the business of green living, will developed into real economic activity during the next decade. Wood, being the only true green construction material, provides us with an opportunity to develop this business as a real competitive advantage. Many countries have, in fact, already noticed this opportunity. For example, Germany expects that the environmental products and services will cover as much as 15% of its GDP until 2020.

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Chemical Analysis and Toxic Hazard of Leachates from Furfurylated Wood

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ABSTRACT

Modification of wood with furfuryl alcohol or furfuryl alcohol prepolymer leads to a wood product with increased decay resistance, hardness and dimensional stability. In normal application, *i.e.* under Use Class 3 conditions, furfurylated wood can be regarded as non-toxic. This has earlier been demonstrated by toxic hazard tests on water leachates using relevant leaching procedures, *e.g.* the OECD Guideline 313 or the Dutch shower test procedure. These leachates showed slight to no toxicity towards standard aquatic test organisms. However, when using forced leaching procedures with limited amount of water such as the EN 84 procedure, slight to moderate toxicity to the same test organisms was observed, depending on furfurylation process. Furthermore, earlier studies have shown that leachates from wood treated with furfuryl alcohol pre-polymers have higher toxicity to *Vibrio fischeri* (luminescent marine bacterium) than leachates from wood treated with furfuryl alcohol monomers and that this probably is attributed to differences in leaching of chemical compounds. The ambition of the present study, was to investigate which chemical compounds in the leachates causes toxicity to the aquatic organisms *V. fischeri* and *Daphnia magna* (water flea). In this study five different wood species, both hardwoods and softwoods, treated with three different furfurylation processes, were leached according to two different leaching methods. The study shows that this difference in toxicity of leachates towards *V. fischeri* most likely cannot be attributed to maleic acid, furan, furfural, furfuryl alcohol or 2-furoic acid. However, the difference in toxicity might be caused by the substance 2,5-furandimethanol. Leachates from furfurylated wood still need to be investigated further in order to identify the chemical differences between wood furfurylated with furfuryl alcohol monomers and furfuryl alcohol prepolymer causing differences in toxicity to different organisms.

INTRODUCTION

The demand for timber products is increasing with global population and affluence (Militz and Lande 2009). Concerns regarding conventionally used toxic wood preservatives and the deforestation of tropical forests have become more prominent both socially and politically (Lande *et al.* 2008). Wood based products are generally recognised as an environmentally favourable raw material. New and innovative wood products with extended service life can be expected to contribute to increased carbon dioxide (CO₂) storage (Gustavsson *et al.* 2006b). An improved competitiveness of wood

based building material might also result in decreased consumption of greenhouse gas intensive building materials such as concrete, steel and aluminium (Schulz 1993).

Environmentally more benign methods are warranted for wood protection in the future. The conventionally used toxic wood preservatives have become an issue within the environmental acceptability of biocides in general (Lande *et al.* 2008). Chromated copper arsenate (CCA) that has been extensively used for several decades is now subject to limitations concerning production and use (KIFS 1998, Hingston *et al.* 2001, Ibach 2005, Townsend *et al.* 2005). In 2004, the United States Environmental Protection Agency (EPA) prohibited CCA for products for any residential use including playground equipment, decking, and outdoor furniture (Ibach 2005). Consequently, there is a desire to develop wood protection systems with improved environmental acceptability such as modified wood and chromium and arsenic free biocides.

Ecotoxicological studies focusing on determining the toxic hazard of wood treated with conventional preservatives of different types, including naturally durable and semi-durable wood species, were carried out in the late 1990s (Van Eetvelde 1998, Van Eetvelde *et al.* 1998). In these studies it was concluded that the main impact during service life was not due to emissions to soil but to water and subsequently aquatic organisms. Leachates from furfurylated wood have in several studies, with a variety of leaching methods, been shown to have very low toxicological effects (Van Eetvelde *et al.* 1998, Van Eetvelde 1998, Epmeier *et al.* 2004, Lande *et al.* 2004a, Lande *et al.* 2004b, Treu *et al.* 2009, De Vetter *et al.* 2009, Pilgård *et al.* 2010a, Pilgård *et al.* 2010b). Pilgård *et al.* (2010a) used the leaching method OECD Guideline 313 (2007) and the shower test method (Haverman *et al.* 1993) and found a low toxicity of leachates from furfurylated wood to both *Vibrio fischeri* and *Daphnia magna*. They also found a higher toxicity of leachates from wood furfurylated with a furfuryl alcohol prepolymer than of the leachates from wood furfurylated with a furfuryl alcohol monomer. They draw the conclusion that this difference most like can be attributed differences in leached chemical compounds. De Vetter *et al.* (2009) and Pilgård *et al.* (2010b) used the harsher leaching method EN 84 (1996) and an increase in toxicity of leachates from furfurylated wood compared to the two milder leaching methods OECD Guideline 313 (2007) and the shower test method could be seen. To increase the understanding of the toxic behaviour of the leachates chemical analysis are often needed to explain the toxicity results.

Wood modification is an alternative to protection of wood with toxic chemicals. Wood modifications do not have a toxic mode of action as is the case for preservative treated wood (Hill 2006). 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 following disposal or recycling of the modified wood (Hill 2006). The wood constituents can be chemically altered and/or the wood structure can be physically altered. Both of these changes can lead to more durable wood (Hill 2006).

Furfurylation is a wood modification using the modification chemical furfuryl alcohol obtained from hemicellulose rich agricultural waste, such as corn cobs or sugar cane residuals (Lande *et al.* 2008, Chuang *et al.* 1984, González *et al.* 1992, González *et al.* 2002, Maciel *et al.* 1982). Furfuryl alcohol molecules can, due to its polarity, penetrate into the wood cell wall and polymerize *in situ*. This results in a permanent swelling of the wood cell walls (Stamm 1977). Furfurylation of wood leads to high protection

against bio degradation by fungi, bacteria, and marine borers (Lande *et al.* 2004a) and it also improves the hardness, lowers the equilibrium moisture content (Epmeier *et al.* 2004) and significantly improves the dimensional stability of the wood (Westin 2004). Anti shrinking/swelling efficiency has been reported to range from 30 to 80% depending on chemical formulations and wood species used (Homan and Jorissen 2004, Westin 2004, Lande *et al.* 2004b).

EXPERIMENTAL

Process conditions

The material was modified according to one of the treatments A, B or C (Table 1). After treatment the materials were leached according to one of the two leaching methods European Standard EN 84 (1996) or the OECD Guideline 313 (2007). One set of samples were also subjected to extraction with dichloromethane.

Table 1: Treatment and process conditions

Treatment	Process conditions
Treatment A	Full cell impregnation with a 30 % furfuryl alcohol solution followed by vacuum drying, curing by steaming and finally kiln drying
Treatment B	Full cell impregnation with a 40 % furfuryl alcohol solution followed by vacuum drying, curing by steaming and finally kiln drying
Treatment C	Full cell impregnation with 20 % furfuryl alcohol prepolymer followed by kiln drying and finally high temperature curing/drying

Wood material

Solid boards made of hardwood species *Fagus sylvatica* and *Fraxinus excelsior*, softwood species *Pinus radiata* and Southern Yellow Pine were used. These materials were modified with treatment A or treatment B according to the process conditions and yielded WPG as summarized in Table 2. After treatment, the boards were cut into samples with the dimensions of 15 x 25 x 50 mm (R × T × L). The material was then leached according to European Standard EN 84 (1996) and maleic acid analysis was conducted.

Table 2: Treatment, leaching procedure and weight percent gain (WPG) of the wood species Pinus radiata, Fagus sylvatica, Fraxinus excelsior and SYP.

Treatment	Leaching procedure	Weight percent gain (%)			
		<i>P. radiata</i>	<i>F. sylvatica</i>	<i>F. excelsior</i>	SYP
Treatment A	European Standard EN84 (1996)		18.7	14.2	42.7
Treatment B	European Standard EN84 (1996)	41.8	31.2	18.2	40.2

A second set of samples was leached according to the OECD Guideline 313 (2007, Table 3). Solid boards (50 x 100 x 4000 mm) of *Pinus radiata* and *Pinus sylvestris* where treated with either treatment B or treatment C according to the process conditions and yielded WPG as summarized in Table 3, cut in pieces of 15 x 70 x 150 mm (R × T × L) and end-sealed. The material from *P. radiata* was planed prior to treatment because of suspected biocide surface treatments (anti-sap stain agents). The material from *P.*

sylvestris was, as in commercial treatment procedures, planed after treatment. After treatment the samples were leached.

Table 3: Treatment, leaching procedure and weight percent gain (WPG) of the two wood species *Pinus sylvestris* and *Pinus radiata*.

Treatment	Leaching procedure	Weight percent gain (%)	
		<i>P. sylvestris</i>	<i>P. radiata</i>
Treatment B	OECD Guideline 313 submersion procedure	37.4	57.2
Treatment C	OECD Guideline 313 submersion procedure	17.2	22.9

A third set of samples, *Fagus sylvatica* and *Pinus sylvestris* furfurylated with treatment B, were analyzed with regard to solvent extractable compounds. Oligomers were extracted from the wood with dichloromethane by AKZO NOBEL Industrial Coatings A/S, Copenhagen, Denmark.

Leaching methods

European Standard EN 84

The leaching was done according to European Standard EN 84 with 10 water changes during 14 d in demineralized water with a water-over-wood-volume equalling 5. The samples had the dimensions of 15 x 25 x 50 mm (R × T × L). Leaching water was collected after 1 d, 7 d, and 14 d. These leaching waters were then used for the analyses of furfuryl alcohol content.

OECD Guideline 313, submersion procedure

End-sealed specimens (15 x 70 x 150 mm (R × T × L)) larger than the standard recommends were used but the recommended ratio (0.4 cm²/ml) between the surface of the wood and the amount of water was kept. The submersion test was continued for 32 d with demineralized water, during which the water was replaced eight times at set intervals. The leachates were collected after 0.25, 1, 2, 4, 6, 8, 15, 22, and 32 d. These leaching waters were then used for the analyses of content of furan compounds.

Chemical analysis

Furan compound analysis

The leaching water from the furfurylated samples leached according to European Standard EN84 were analyzed for furfuryl alcohol content according to an internal standard method using a high-performance liquid chromatography instrument (HLP25200 Merck HPLC System). The high-performance liquid chromatograph was equipped with a photo diode array detector.

The leaching water from the furfurylated samples leached according to the OECD Guideline 313 submersion procedure were analyzed for the presence of furan compounds by using a high-performance liquid chromatography instrument (Waters Pharmaceutical Division, Milford, MA, USA). It consisted of a Waters 996 photo array detector and a Waters 2487 dual absorbance detector, a Waters 600 controller quaternary pump with a thermo stable column area, and a Waters 717 auto sampler, operating with the Waters Empower™ 2 Software. The furan compounds were separated using a X-Bridge® C18 reversed phase column (5µm) 3.0 mm × 150 mm +

3.0 mm × 20 mm guard column (5µm). Unknown compounds were evaluated using mass spectrometry Thermo Finnigan LCQ Deca XP apparatus (Thermo Finnigan, LC-MS Division, San Jose, CA, USA). This consisted of an UV detector, Electro Spray Ionization or Atmospheric Pressure Chemical Ionization source and ion trap mass spectrometry detector, operating with the Xcalibur software 2.0 SR2.

Maleic acid analysis

This acid was analyzed because the maleic anhydride catalyst is expected to hydrolyze into maleic acid in the modification process. The leaching water from the furfurylated samples, leached according to OECD Guideline 313 submersion procedure, was analyzed for the presence of maleic acid using a high-performance liquid chromatography instrument (Agilent Technologies 1200 Series). The liquid chromatograph was equipped with a UV – 230 nm detector. The chromatographic separations were done with an Agilent Technologies Eclipse XDB-C18, 5 µm, 4.6x150 mm auto-sampler.

Rest monomer analysis

The compounds extracted with dichloromethane were analysed with gas chromatography (GC/FID) and mass spectroscopy (GC-MS) by AKZO NOBEL Industrial Coatings A/S, Copenhagen, Denmark.

RESULTS AND DISCUSSION

Chemical analysis of water leachates

The chemical analysis of the leachates from furfurylated wood, leached according to the OECD Guideline 313, showed that wood furfurylated with treatment B leaches in general more maleic acid than wood furfurylated with treatment C (Table 4). This means that maleic acid is most likely not the reason why the leachates from wood furfurylated with treatment C are in general more toxic to *V. fischeri* than the leachates from wood furfurylated with treatment B. On the other hand the amount of leached 5-hydroxymethylfurfural (HMF) together with 2,5-furandimethanol (BHMF) is higher in the leachates from wood furfurylated with treatment C than from treatment B. BHMF was present in the formulation for treatment C and it is maybe more likely that it was this compound that was detected in the leaching water and not HMF. This compound may account for the higher toxicity of leachates from wood furfurylated with a prepolymer than with monomers but this need to be further investigated.

Table 4: Chemical compounds leached from *Pinus sylvestris* and *Pinus radiata* modified with different treatments during leaching according to the OECD Guideline 313, submersion procedure.

Treatment	Wood species	0.25 days					15 days				
		Furfural (mg/L)	Furfuryl alcohol (mg/L)	2-Furoic acid (mg/L)	HMF ^a + BHMF ^b (mg/L)	Maleic acid (mg/L)	Furfural (mg/L)	Furfuryl alcohol (mg/L)	2-Furoic acid (mg/L)	HMF + BHMF (mg/L)	Maleic acid (mg/L)
Treatment B	<i>P. sylvestris</i>	1.37	0.34	0.15	0.15	4.5	0	1.75	5.62	1.33	19.35
	<i>P. radiata</i>	0.49	0.19	0	0.07	1.03	0.51	1.59	10.08	1.52	9.62
Treatment C	<i>P. sylvestris</i>	0.12	0	0	0.40	1.67	0	0.62	0.94	2.97	5.33
	<i>P. radiata</i>	0.11	0.00	0	0.66	2.39	0.16	0.36	0.38	3.39	6.97
Control	<i>P. sylvestris</i>	0.07	0	0	0	-	0	0	0	0	-
	<i>P. radiata</i>	0	0	0	0	-	0	0	0	0	-

^a5-hydroxymethylfurfural

^b2,5-furandimethanol (bis-hydroxymethylfurfural)

^cBelow detection limit

The results from the chemical analysis using European Standard EN84 leaching water from treatment B treated samples showed that *F. sylvatica* had the highest amounts of leached furfuryl alcohol during the test series (Figure 1). The only wood specie that decreased in furfuryl alcohol leaching was *P. radiata*. Lande *et al.* (2004b) found an average leaching value for furfurylated *P. sylvestris* (weight percent gain 30%) of 0.23 mg/L that is 50 times lower than the highest value for *F. sylvatica* found in the present study. The reason for this could be the higher weight percent gain of the furfurylated wood samples in the present study (except for *F. excelsior*) but more likely it is due to different treatment conditions. No decrease in amount of leached furfuryl alcohol could be seen for any of the wood species, except for a slight decrease for *P. radiata*. These findings support an earlier toxic hazard study on furfurylated wood (De Vetter *et al.* 2009).

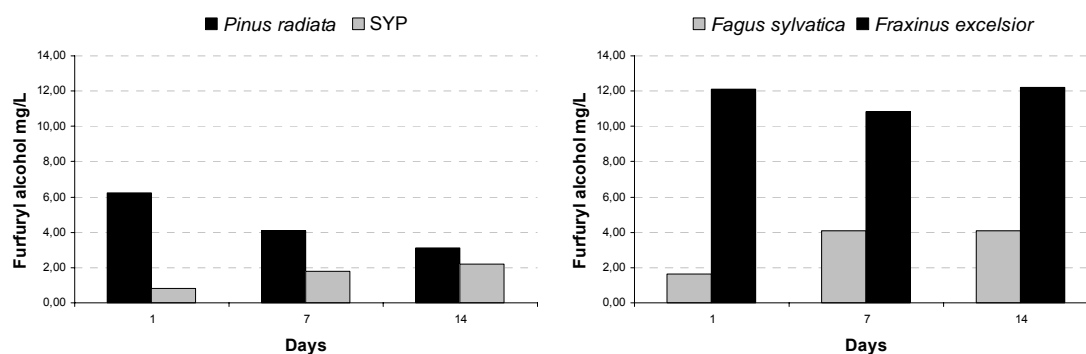


Figure 1: Amount of leached furfuryl alcohol in mg/L after leaching according to European Standard EN84 (1996). Left: the softwood species Southern Yellow Pine (SYP) and *Pinus radiata* and right: the hardwood species *Fagus sylvatica*, *Fraxinus excelsior*.

Chemical analysis of dichloromethane extraction

The chemical analysis of the dichloromethane extracted compounds from furfurylated wood showed that a higher amount of all the tested chemicals were extracted from *P. sylvestris* than from *F. sylvatica*. Since these compounds are extractable with solvents they will most unlikely play a big part in the toxicity of the water leachates from furfurylated wood during service life.

Table 5: Chemical compounds extracted from *Pinus sylvestris* and *Fagus sylvatica* during leaching with dichloromethane.

Chemical compound	<i>Pinus sylvestris</i> (mg / m ²)	<i>Fagus sylvatica</i> (mg / m ²)
Furfuryl alcohol	650	400
Furfural	200	120
Methylfuranone	200	150
Furylmethylfuran	700	200
Difurfurylether	1000	400
Difurfurylfuran	1200	500
Unknown furfuryl compound	500	150
Unknown furfuryl compound	800	300

CONCLUSIONS

Toxicity analysis shows that the choice of leaching method and toxicity test is decisive for the outcome of the test. The harsher leaching method, the EN 84, gives the highest toxic values for furfurylated wood compared to other milder leaching methods (Van Eetvelde *et al.* 1998, Van Eetvelde 1998, Meier *et al.* 2004, Lande *et al.* 2004b, Lande *et al.* 2004c, Treu *et al.* 2009, De Vetter *et al.* 2009, Pilgård *et al.* 2010a, Pilgård *et al.* 2010b). This is something that needs to be taken into consideration each time toxicity is monitored and evaluated. The present study found that maleic acid is most likely not the reason why the leachates from wood furfurylated with a prepolymer solution are in general more toxic to *V. fischeri* than the leachates from wood furfurylated with a monomer solution. However, the difference in toxicity might be caused by the substance 2,5-furandimethanol which was found in higher amounts in the leaching waters from wood furfurylated with a prepolymer solution. The present study also found that under EN 84 leaching, *F. sylvatica* treated with a 40% furfuryl alcohol monomer had the highest amounts of leached furfuryl alcohol compared to *P. radiata*, *F. excelsior* and SYP. Most of the compounds found after dichloromethane extraction will most unlikely play a big part in the toxicity of the water leachates from furfurylated wood during service life. Leachates from furfurylated wood still need to be investigated further in order to identify the chemical differences between wood furfurylated with furfuryl alcohol monomers and furfuryl alcohol prepolymer causing differences in toxicity to different organisms.

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Electron Beam Initiated Polymerization of Poly(ethylene glycol) Based Wood Impregnants

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Keywords: Electron beam, wood, polymerization, impregnation, moisture, dimensional stability

ABSTRACT

The current study demonstrates that methacrylate and acrylate poly(ethylene glycol) (PEG) functional oligomers can be effectively impregnated into wood blocks, and cured efficiently without catalyst by e-beam radiation, allowing for less susceptibility to leaching, swelling, and favourable properties including increased density and higher Brinell hardness values. PEG based monomers were chosen because there is a long history of this water soluble monomer being able to penetrate the cell wall, thus bulking it and decreasing the uptake of water which further protects the wood from fungal attack. (Glaser *et al.* 1999) Diacrylate, dimethacrylate, and dihydroxyl functional PEG of Mw 550, of concentrations 0, 30, 60, and 100 wt% in water, were vacuum pressure impregnated into Scots Pine blocks of 15 x 25 x 50 mm in an effort to bulk the cell wall. The samples were then irradiated and compared with non-irradiated samples. It was shown by IR, DSC, and TGA that the samples were fully cured and more thermally stable. Leaching studies indicated a much lower amount of oligomer loss from the cured vinyl functional PEG chains in comparison to hydroxyl functional PEG indicating a high degree of fastening of the polymer in the wood. The Brinell hardness indicated a very large difference in the e-beam cured samples compared to the samples of hydroxyl functional PEG and un-cured vinyl PEG samples which actually became softer than the untreated Scots Pine.

INTRODUCTION

Since the 1950s, electron beam radiation, involving the transfer of energy from electrons as they penetrate matter, for use in initiation of free radical polymerization has been explored enthusiastically by researchers and entrepreneurs alike. (Rodrigues 1987). E-beam has also been demonstrated for use in curing conventional composites where thick samples can be cured in which much lower temperatures are reached due to room temperature curing with the only heat generated being that of the exotherm of polymerization, making for a more controlled process and reduction of thermal degradation. (Wallström and Lindberg 1999). It has not yet been explored if PEG of higher molecular weights is methacrylate and acrylate functional if it is able to enter the

cell wall and provide the characteristics that PEG alone can without leaching out over time due to crosslinking. This study examines the impregnation degree, feasibility of e-beam cure, and dimensional stability of vinyl functional PEG in comparison to non-reactive PEG polymer impregnation.

EXPERIMENTAL

Materials

All samples were cut from the same plank of Scots Pine, *Pinus Sylvestrus* sapwood with a density of 526 kg m⁻³ and a moisture content of 11%. Poly(ethylene) diacrylate (DA-PEG) and poly(ethylene glycol) dimethacrylate (DM-PEG) of Mw 550 and poly(ethylene glycol) (PEG) of Mw 550 were purchased from Sigma Aldrich. Impregnation solutions of the three oligomers, PEG, DM-PEG, and DA-PEG were prepared by mixing them with water in 0, 30, 60, and 100 wt % solutions. 0 % consisted only of de-ionized water and 100% of only oligomer. An example formulation of 60 % DM-PEG: 180 g DM-PEG and 120 g de-ionized water.

Methods

Sets of 10 wooden blocks, that had been conditioned at 65% RH at 20°C (m65%RH) weighed and dimensionally measured (v65%RH) , were placed in 1 L autoclaves and weighted down in order to ensure homogeneous coverage of impregnation solution. The impregnation solution was then added with a funnel and 10 bars of oxygen for 2 hours to ensure complete polymer impregnation into the blocks, observed by sawing through representative blocks.

Wood samples moisture content was determined according to ISO 3130. Moisture content was found to be 11% ± 1%.

The moisture content of the modified samples (MC_m) after 14 d in water was calculated using Eqn. 1. In Eqn. 1, m₁ is the amount of polymer that leached from the sample over 14 days, and w₃ is the weight of the wet samples after 14 days in water.

$$MC_m = \frac{m_1 - m_2}{m_3} \times 100 \quad (1)$$

Half of the samples were not e-beam cured, but directly placed in the vacuum oven for 48 h at 50°C then weighed and the dimensions measured in order to determine the WPG of polymer and the swelling induced by the polymer. The other half was first e-beam cured and then placed in the same vacuum oven under the same conditions for 48 h, weighed and dimensions recorded. The oligomers were not observed to volatilize under these conditions, however the uncured samples did lose a fraction of monomer that flowed out of the wood blocks due to the reduced pressure.

Leaching studies were performed over 14 days in water according to EN 84-accelerated ageing of treated wood prior to biological testing.

Volume was measured using pneumatic callipers, width, length, and thickness with micrometer accuracy. Volumetric shrinkage or swelling was found using ISO standard 4858 and 4860 on equipment that can measure to the hundredths place 0,01.

EB curing was performed with a pulsed sweeping electron beam, produced by a microtron accelerator with an energy of 6.5 MeV and a current of 80 mA. The dose was 10 MRa and was calibrated with a Risø calorimeter. The samples were cured in plastic bags under atmospheric conditions to prevent any evaporation.

Brinell hardness was performed using a Alwetron TCT50 Universal Testing machine with a load cell of 5 kN with a steel ball of 10 mm and a test force of 50 kp according to standard EN-1534. The average of 10 repeats is presented.

The anti-swelling efficiency was calculated of the treated samples after soaking 14 days in water using Equation 2, where S_n is the swelling of the untreated sample and (S_t) is the swelling of the treated sample.

$$ASE\% = \left(\frac{S_n - S_t}{S_n} \right) \times 100 \quad (2)$$

The moisture exclusion efficiency (MEE%) was calculated after soaking the samples for 14 days in water using Equation 3, where MC_{nm} is a measure of the moisture content of the untreated wood block and MC_m is the moisture content of the treated samples.

$$MEE\% = \left(\frac{MC_{nm} - MC_m}{MC_{nm}} \right) \times 100 \quad (3)$$

The samples and their names used in this text are listed in Table 1.

Table 1: Naming Scheme of Samples

Sample impregnated with polymer:	Uncured blocks	Cured blocks
PEG	UC-PEG	EB-PEG
DM (dimethacrylate PEG)	UC-DM	EB-DM
DA (diacrylate PEG)	UC-DA	EB-DA

RESULTS AND DISCUSSION

The cured and uncured samples were weighed after drying in the vacuum oven to determine the amount of polymer taken up by the blocks (Figure 1.). It was found that there was a large increase in polymer uptake from 30 to 60 wt%, but from 60 to 100 wt% there was not much difference, which may be due to the viscosity of the monomer solution.

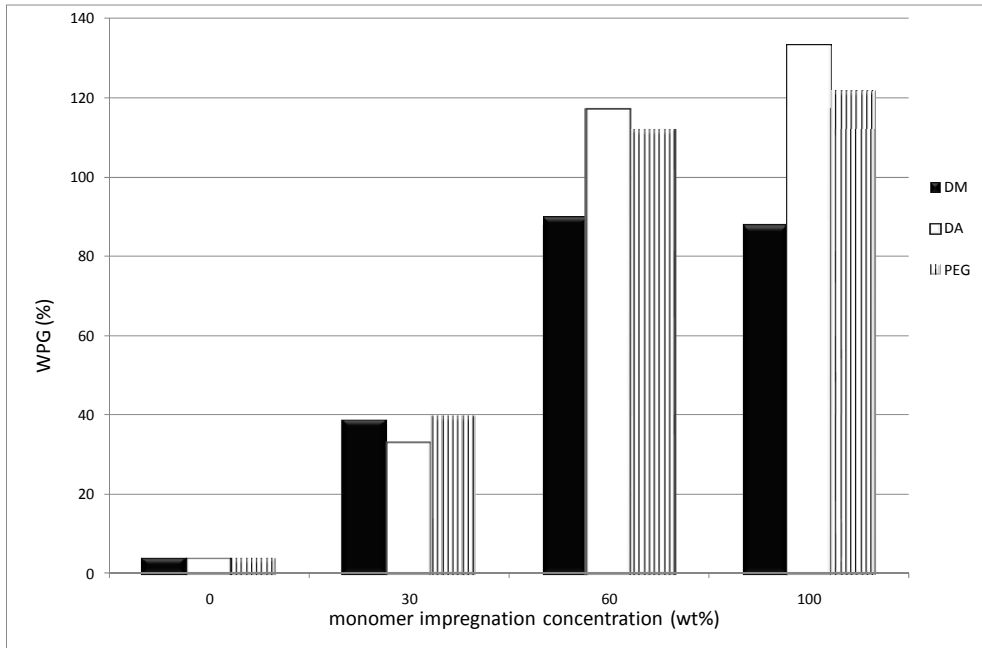


Figure 1: WPG of polymer in wood blocks after impregnation and before cure.

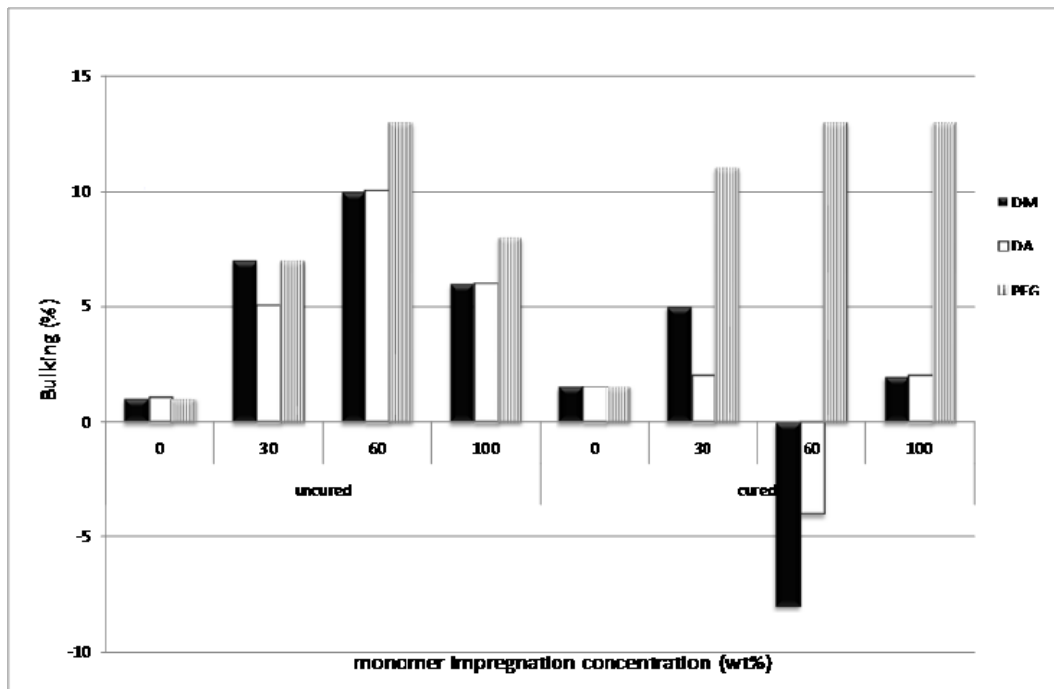


Figure 2: Bulking of uncured and cured samples.

Dimensions decreased in all samples after cure in comparison to the uncured samples with the exception of PEG, while shrinking was observed in the 60 wt% polymer samples in comparison to the reference. (Figure 2.) This is attributed to the cure shrinkage of the polymers and indicates that 60 wt% could penetrate the cell wall best. The samples were placed in water for 14 days in order to determine moisture content and leaching of monomer over this time (Figure 3.).

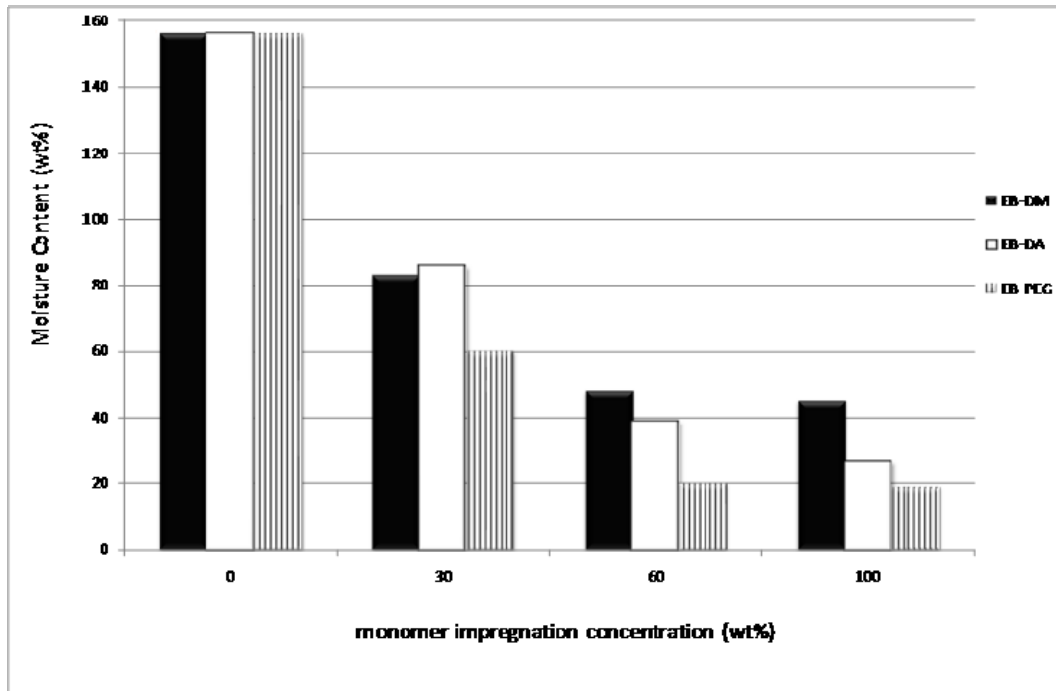


Figure 3: Moisture Content of the e-beam samples after 14 d in water.

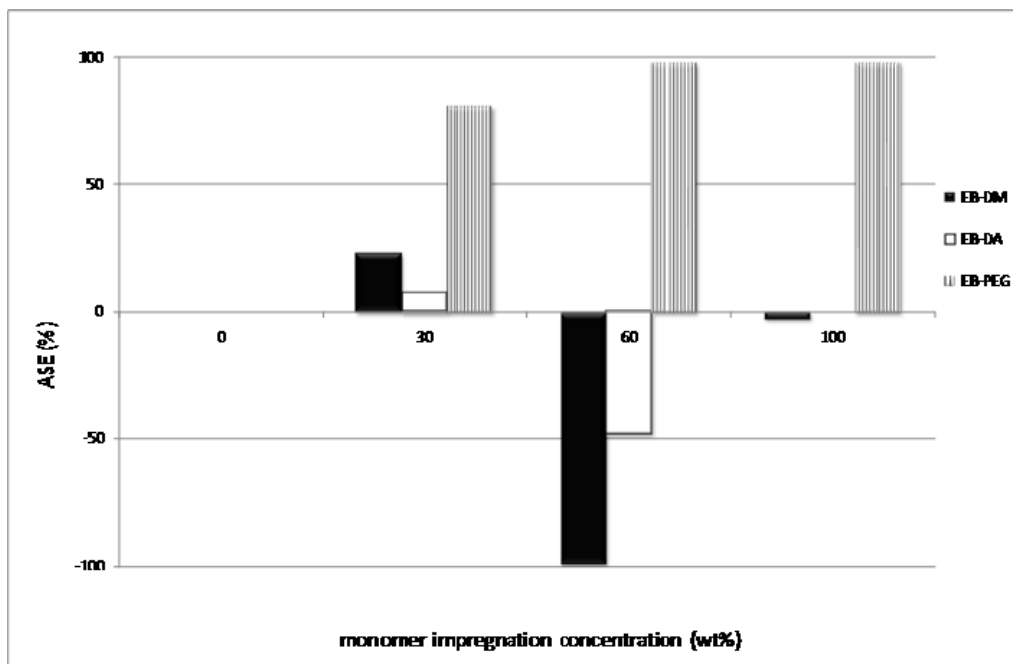


Figure 4: ASE% of e-beam treated samples after 14 days in water.

It was found that there was a large increase in polymer uptake from 30 to 60 wt%, but from 60 to 100 wt% there was not much difference, which may be due to the viscosity of the monomer solution. The ASE% was very poor and even negative in the samples in which cure shrinkage was observed which may have been due to more open space in the cell wall with contraction of the monomers (Figure 4). All PEG samples showed relatively good ASE% as expected. Moisture exclusion efficiency % increased with the WPG of polymer illustrating that as the space became filled with polymer less weight of water was absorbed (Figure 5).

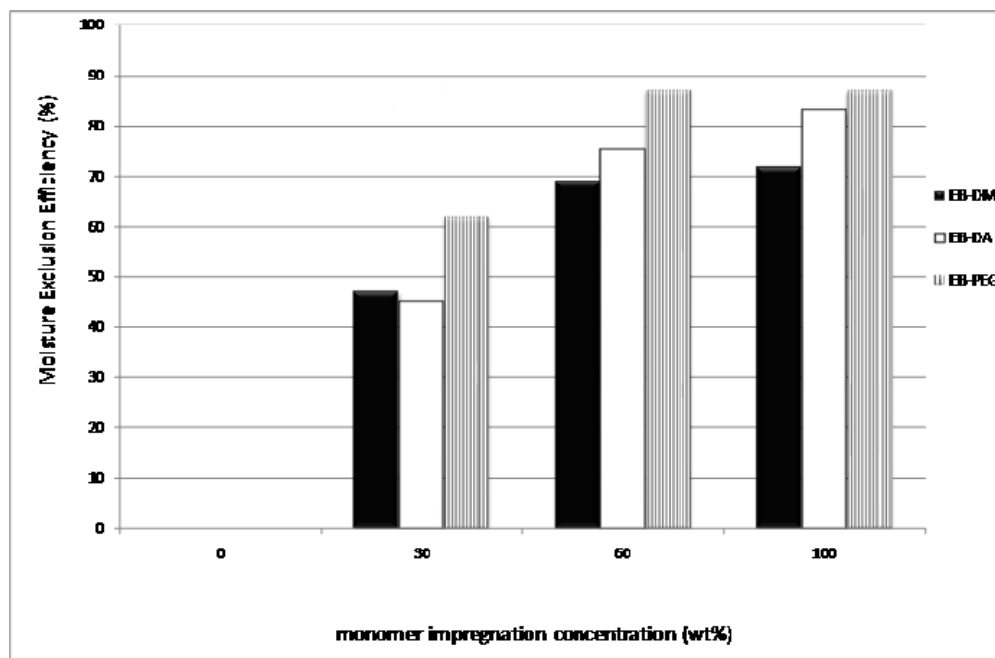


Figure 5: Moisture Exclusion Efficiency % of e-beam samples after 14 days in water.

CONCLUSIONS

This research opens the door to an efficient, less expensive, and cleaner method to bind reactive vinyl oligomers into wood.

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Microscopic and Spectroscopic Methods for Investigation of Wood Modified with Chitosan

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Keywords: Chitosan, microscopy, confocal, Raman spectroscopy, osmium tetroxide.

ABSTRACT

This paper evaluates several microscopic and spectroscopic techniques that have been used to determine location and distribution of chitosan and chitosan derivatives in modified wood material. In particular, localisation of chitosan within wood is of interest due to the importance of modifying the cell wall for improving key target properties, such as stiffness and dimensional and conformational stability. With the development of many different instrumental techniques with increasing resolution and power, the level of detail that is now possible facilitates understanding at the molecular level on the outcomes of experimental wood modifications. This paper uses the example of chitosan-modified radiata pine sapwood with emphasis on the level of detail that is obtainable when a number of microscopic and spectroscopic techniques are used in combination.

INTRODUCTION

Commercial chitosan is a random co-polymer of (poly(1→4)-N-acetyl-2-amino-2-deoxy-β-D-glucopyranose), and (poly(1→4)-2-amino-2-deoxy-β-D-glucopyranose) in a ratio *ca* 1:4. Chitosan is obtained from N-deacetylation of chitin, and the number of residual N-acetyl groups of the (poly(1→4)-2-amino-2-deoxy-β-D-glucopyranose) polymer effects its physical and chemical properties, including the polymer modulus (Nishino *et al.* 1999) and bioactivity. Modification of wood material with commercial chitosan has potential to alter both the stiffness (Torr *et al.* 2006) and biological durability properties (Torr *et al.* 2005; Larnøy *et al.* 2006; Singh *et al.* 2008), provided that the chitosan material and formulation carrying the chitosan preparation can penetrate the wood cell wall. To enable this, it was shown to be necessary to hydrolyse commercial chitosan to low molecular weight, water-soluble oligosaccharides (Torr *et al.* 2006). This conversion could be carried out using enzymatic and acid-catalysed hydrolysis and, specifically for chitosan, by nitrous acid de-aminative de-polymerisation (Allan and Peyron 1997). This produced a range of chitosan oligomer preparations of approximately 5-15 anhydro-sugar units in length and therefore of varying molecular volumes with differing capacity to penetrate wood cell walls. Wood materials modified with chitosan oligomers were then subjected to both bulk material mechanical and biological test procedures to determine the effective outcome of the modification (Torr *et al.* 2006).

Deriving fundamental knowledge of why and how a particular chitosan modification was effective in property enhancement is a valuable, iterative learning process that can lead to new modification strategies and procedures that are more effective and/or efficient for the improvement of wood properties. In this example, the location and distribution of chitosan and its oligomers within the wood cell wall was considered

important to correlate molecular distribution and density with the degree of property improvement achieved (Torr *et al.* 2006).

The major challenge to detect and image chitosan and chitosan oligomers in cell walls is to discriminate the carbohydrate structure against a background of lignocellulose (Singh *et al.* 2010). Without any UV-absorbing or fluorescent functional groups, chitosan detection requires specific microscopic or spectroscopic techniques. This paper will describe some of the microscopic and spectroscopic techniques which have been applied to discover fundamental information of the location and distribution of chitosan within the modified wood cell wall matrix.

SUMMARY OF TECHNIQUES

Table 1 shows a summary of some of current methods and techniques, along with those that have potential application to the examination of chitosan-modified wood.

Table 1: Some current and potential microscopic techniques for application to chitosan imaging

Technique	Sample preparation	Information obtained
Fourier transform infrared microscopy	Dried specimen	Distribution of NH ₂ at 3400 cm ⁻¹
Synchrotron radiation	Wet or dried specimen	Changes to crystallinity of cell wall regions due to presence of chitosan crystals
Confocal fluorescence microscopy	Specific chemical reaction of primary amine with fluorophore	Distribution of N-fluorophore assumed to be same as chitosan (Torr <i>et al.</i> 2006)
Osmium tetroxide (OsO ₄) staining with light microscopy, FE-SEM in BEI mode	Specific chemical reaction of OsO ₄ with chitosan primary amine	Distribution of osmium nitrido complex assumed to be same as chitosan (Singh <i>et al.</i> 2010)
Raman microscopy	Wet or dried specimen	Provides chemical and structural information complementary to IR (Figure 2)
SEM-EDX with micro CT (X-ray micro-computed tomography)	Coordination of heavy metal (e.g., Cu, Pd) to chitosan primary amino group	Detection and distribution of heavy metal, assumed to be same as chitosan
Thermal neutron tomography of ¹⁰ B amine complexes.	Coordination of NH ₂ to ¹⁰ BH ₃	Spatial detection of α-particles from ¹⁰ B neutron capture and transmutation to ⁷ Li, assumed to be same as chitosan distribution.

SELECTED EXAMPLES

Some of the imaging techniques listed in Table 1 have potential to provide high-resolution and specific signals and responses from modified wood material, and provides the researcher with experience in using large and exciting instruments. However, there is still a need for simple day-to-day laboratory microscopy and spectroscopy imaging techniques (Torr *et al.* 2006, Singh *et al.* 2008, Singh *et al.* 2010). Light microscopy of specimens of wood modified with chitosan without any specific chitosan staining or modification was useful only for detection of chitosan in cell

lumens. Figure 1 shows a micrograph of such an image, where the chitosan material appears orange-yellow (as darker patches here) against the background of wood cells.

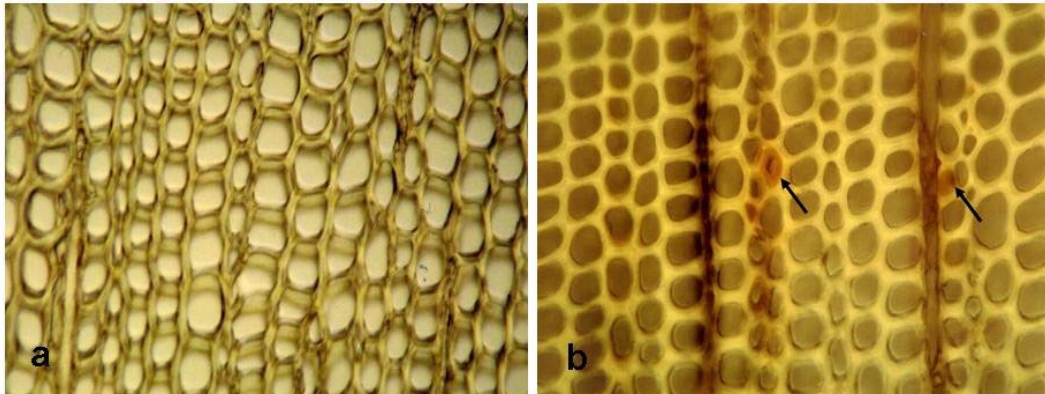


Figure 1: Light micrograph of (a) radiata pine sapwood, and (b), chitosan modified wood (Singh *et al.* 2008).

Without specific modification of chitosan, both infrared and Raman microscopy did not produce sufficient discrimination of chitosan against a background of lignocellulose. Figure 2 shows the Raman spectrum (546 nm laser) obtained for a chitosan-modified wood specimen compared with the Raman spectrum of natural wood, showing almost no difference between the two spectra.

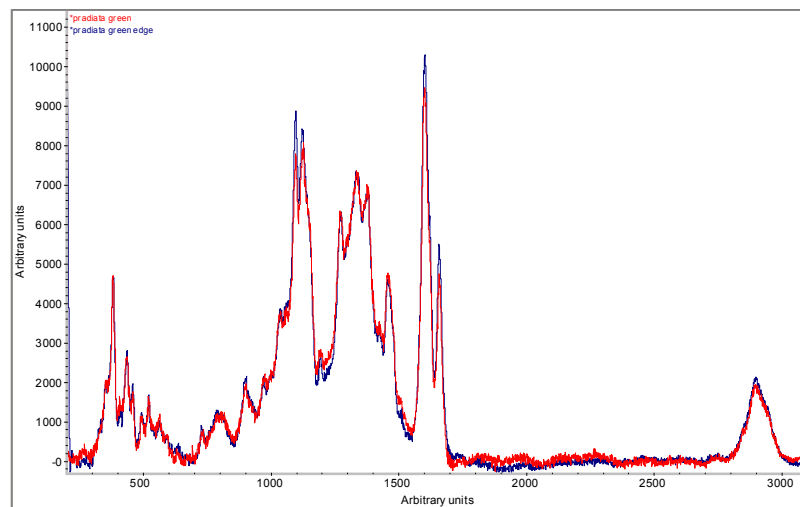


Figure 2: Raman spectra of unmodified cell wall and chitosan-modified cell-wall superimposed.

Light microscopy of sections cut from chitosan modified wood and stained with aqueous toluidine blue using standard techniques showed uniform distribution of stain reaction distribution of natural wood, and lesser intensity of stain in regions of cell wall associated with appearance of chitosan in cell lumens. Here, inhibition of the stain reaction intensity is interpreted as regions of cell walls having been modified with chitosan (Figure 3, Torr *et al.* 2006). This technique has potential for discriminating chitosan distribution by using several different cell-wall reactive stains, such as those specific for cell wall lignin.

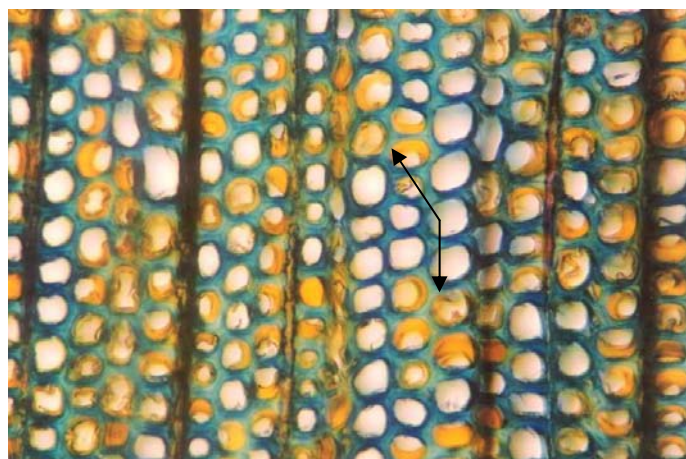


Figure 3: Light micrograph of chitosan modified wood stained with toluidine blue (Torr et al. 2006, reprinted with permission from New Zealand Journal of Forestry Science © Scion, www.scionresearch.com/nzjfs)

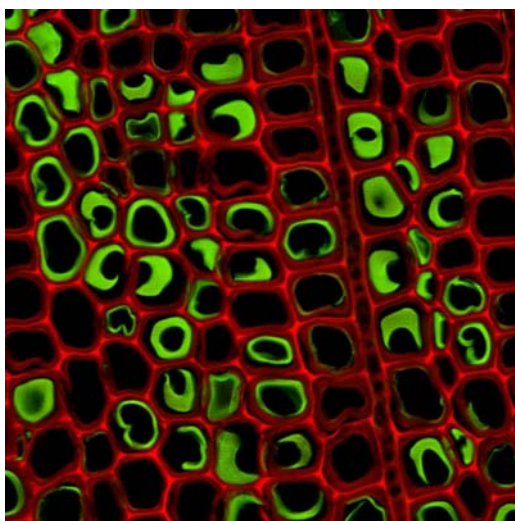


Figure 4: Confocal fluorescence micrograph of melamine-derivatised chitosan modified wood (Torr et al. 2006, reprinted with permission from New Zealand Journal of Forestry Science © Scion, www.scionresearch.com/nzjfs)

Confocal fluorescence microscopy of chitosan modified with hydroxymethylmelamine to form a methylene-bridged nitrogen aromatic fluorophore readily showed fluorescent material in cell lumens, but could not distinguish a fluorescence emission spectrum different from that of lignin auto-fluorescence, and therefore did not provide a useful technique for chitosan distribution (Figure 4, Torr *et al.* 2006). A different selection of fluorophore with an emission spectrum well-separated from that of lignin auto-fluorescence has potential to improve this technique.

Sections of chitosan-modified wood material were also reacted with aqueous osmium tetroxide and then examined with the light microscope and also the scanning electron microscope (Singh *et al.* 2010). Osmium tetroxide is a powerful oxidising chemical and also has rich coordination chemistry where ligands with non-bonding electron pairs, such as amines, form well-defined complexes with the metal atom (Cotton and Wilkinson, 1962). Osmium tetroxide is well-known as a specific chemical reagent to

add to carbon-carbon double bonds to form *cis*-hydroxyl complexes and products. In lignocellulose, the majority of carbon atoms in the material already bear an hydroxyl functional group (in cellulose and hemicelluloses) and therefore osmium tetroxide would be expected to be inert to these molecules.

Osmium tetroxide can therefore be regarded as a specific reactant for chitosan owing to the NH_2 group donating the N non-bonding electron pair to osmium (Figure 5), which can then result in an oxidation reaction within the coordination complex to form an osmium-nitrogen multiple bonded product, which has a strong UV and visible absorption spectrum and a dark-coloured appearance (Singh *et al.* 2010).

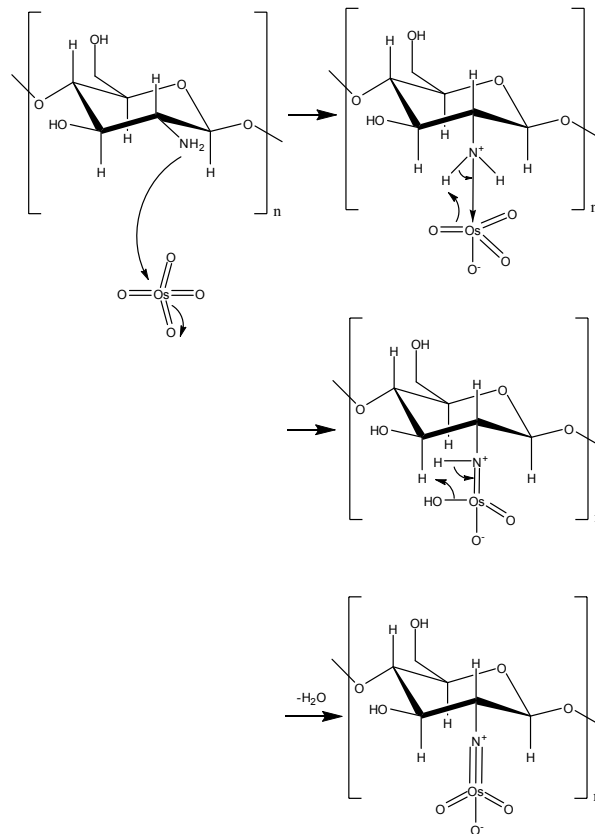


Figure 5: Proposed reaction of chitosan with osmium tetroxide to form chitosan-osmium nitrido derivative.

Chitosan modified wood material reacted with osmium tetroxide was examined by light microscopy and showed excellent discrimination of darkly-stained cell walls. Cell walls that were light-coloured were presumed to be un-modified (Singh *et al.* 2010). Osmium tetroxide treated sections were also examined with field emission scanning electron microscope (FE-SEM), using backscattered electron imaging which is useful for differentiating heavier atoms, such as osmium. As the chitosan-osmium complex appeared much brighter than unmodified cell walls, its distribution within the modified wood cell walls could be examined at far greater resolution than that achievable with the light microscope (Singh *et al.* 2010).

The combined use of the microscopy techniques combined with spectroscopy detection and specific chemical reactions or staining methods have provided complementary information revealing chitosan distribution within the modified wood tissues at high

resolution. Ability to specifically image chitosan in the cell wall has enabled a means for quantifying improvements in chitosan derivatives and formulation chemistry in order to maximise wood modification outcomes.

CONCLUSIONS

Combination of microscopic and spectroscopic techniques specific for chitosan and its oligomers has allowed direct evidence for the presence and location of chitosan in modified wood, especially within cell walls. Improvements to wood material stiffness and biological durability require extensive cell wall modification, and minimal deposition of chitosan in cell lumens.

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Characteristics of Wood Impregnated with Persimmon (*Diospyros* sp.) Extracts

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Keywords: Kaki, kakishibu, polyphenols, biological protection, hydrophobicity, VOC

ABSTRACT

Kakishibu is the juice from unripe persimmons (usually *Diospyros lotus*) that undergoes fermentation for at least 6 months. It is rich in complex polyphenols and has been used in Japan and other Asian countries for centuries as wood stain. It is recognized that kakishibu also increases the durability of wood and that it helps to reduce the "sick building syndrome" by trapping volatile organic compounds. The present work is a first attempt to evaluate quantitatively the effect of impregnation of kakishibu in sensitive species (pine, beech) and to elucidate if a chemical reaction takes place between the polyphenols and wood. Thus, small specimens of pine (*Pinus sylvestris*) and beech (*Fagus sylvatica*) were impregnated under different conditions of vacuum and temperature with kakishibu (Japanese origin, commercial) then dried at 50°C for 3 days. Blank samples for control underwent the same treatment using distilled water instead of kakishibu. Water repellency was evaluated by contact angle measurements on the surface of specimens and on the surface generated after cutting the sample perpendicularly to the first surface. The treated pine samples showed angles as high as 120° that were stable for at least 5 minutes (time of continuous measurement). Blank samples showed initial angles of about 70° but rapidly the water was absorbed in less than 50 seconds. Biological resistance was assessed by using accelerated tests on pine sapwood inspired by EN 113, EN 117, and ENV 807. The results showed no protection against softrot and termites. In the case of Basidiomycetes, there was no protection against *Coniophora puteana* but there was a significant protection against *Poria placenta* and *Gloeophyllum trabeum*. Nevertheless the efficacy evaluated by weight loss was not enough to be considered as efficient as a reference biocide. Finally, pine sawdust was impregnated with kakishibu and dried. It was then exposed to a dynamic nitrogen atmosphere containing propionaldehyde. The kakishibu-impregnated sample was less efficient to trap the aldehyde than the water-impregnated sample. SEM micrographs revealed that kakishibu clogged the lumen in sawdust fibres. The reduction of specific surface can account for the loss in efficacy. A new test is necessary to be carried out on block samples under static and dynamic contaminated atmospheres to clearly assess the power of kakishibu to trap VOC.

INTRODUCTION

Kakishibu is a commercial wood stain sold in Japan and other Asian countries. Since centuries, it has been used in the Far East to confer a beautiful dark brown color to wood and to increase its durability and resistance to decay. More recently, its "natural" image has contributed to its growing popularity. The traditional use of fermented persimmon juice includes also paper and textile treatment to increase their hydrophobicity, rigidity, and durability. Another important benefit has been attributed to kakishibu in recent years: it is popularly recognized that kakishibu-tainted wood can help to heal the "sick building syndrome". This syndrome can occur by the spreading of volatile organic compounds in the air that are used in the glue of particleboards for instance. It can cause different problem for human such as headache, asthma, eye, nose and throat irritation. Hypotheses have been dressed. It is believed that kakishibu is responsible for the trapping of volatile organic compounds responsible of many allergic symptoms. We know that some Japanese studies have been launched but scientific litterature on this topic is not available in peer-reviewed journals. Only iron as pollutant has been studied (Nakajima and Sakaguchi, 2000). This study intends to evaluate quantitatively the change in properties conferred to wood by impregnation or chemical reaction with kakishibu. We selected the change in hydrophilicity, biological resistance and VOC adsorption.

MATERIALS AND METHODS

Materials. A large number of beech and Scots pine sapwood samples (30x10x5 mm) were weighed to select only those showing density values in the narrowest range. They were conditioned for at least one week in a chamber at 20°C and 60%RH. Two kinds of kakishibu were used. Fresh liquid kakishibu (K) and regenerated kakishibu (RK) obtained by dissolving dried kakishibu powder in distilled water at 30 g/l. Both were obtained from a local producer in the Kansai region in Japan and kept at 4°C prior to use. Propionaldehyde >99% was obtained from Aldrich and used as received.

Wood samples treatments. Wood samples were introduced in a glass vessel containing enough K or RK to cover all the wood pieces. A vacuum hose was connected to the vessel to remove air progressively until absence of bubbling. Vacuum was maintained for 2 h in the case of beech and 1 h in the case of pine. Control samples were obtained by impregnation with distilled water. Optionally, the vessel was put to atmospheric pressure than introduced in an oil bath at 90°C for 1 h. For comparison purposes, some untreated samples were directly introduced in hot liquid for 1 h without applying vacuum. In all the cases, the treated samples were put in an air-oven at 50°C for 72 h, which ensured constant weight.

Biological testing. Accelerated screening tests inspired from European standard testing (EN 113, ENV 807, and EN 117) were set by CIDEMCO (Spain) to evaluate the potential resistance of treated samples against Basidiomycetes (*Coniophora puteana*, *Gloeophyllum trabeum*, and *Poria placenta*), softrot (bioactivated soil) and termites (*Reticulitermes* sp.). No ageing was performed on the treated samples. Control (untreated) blocks and samples treated with a reference biocide product were also set for comparison and to validate the test respectively. Before and after the biological testing, the treated samples were conditioned at 20°C and 60%RH for 3 weeks. All the samples were of Scots pine sapwood and measured 30x10x5 mm. They were treated according to the vacuum+heating+drying protocol.

Water repellency. Contact angle was measured with a Digidrop goniometer using 8 μL of HPLC-grade water placed on the surface of the analysed sample. The camera registered automatically the left and right angles of the drop every 2 seconds for up to 5 minutes. Three different samples were used to calculate the average reported value.

VOC adsorption. Propionaldehyde was used as model molecule to study the interaction of treated samples with volatile organic compounds. First, Scots pine sawdust (granulometry 1 mm) was vacuum impregnated with RK or K until saturation. A glass cartridge was filled with the treated sawdust and a flow of dry nitrogen (10 mL/s) was passed for 150 min, which ensured constant weight of the filled cartridge. Then, a bottle containing liquid propionaldehyde was connected to the system as showed in Figure 1 to saturate the nitrogen flow with propionaldehyde vapor at room temperature.

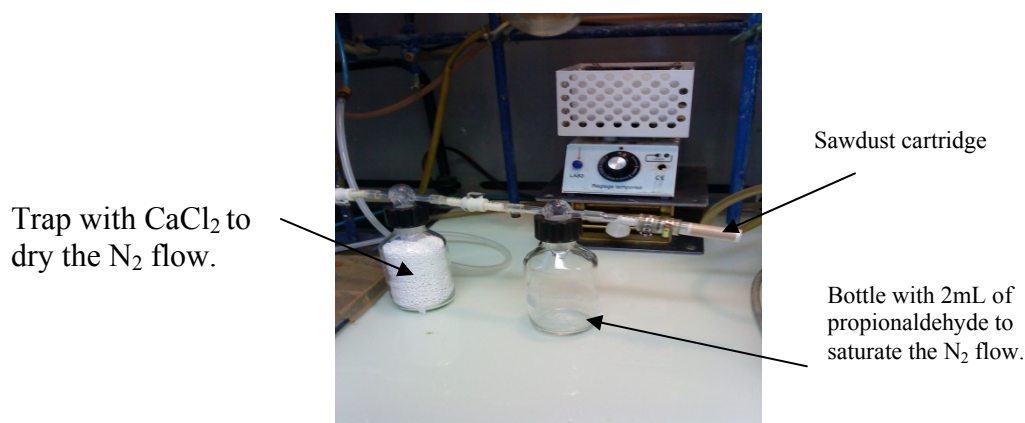


Figure 1: VOC trapping

RESULTS AND DISCUSSION

After all the impregnations, the samples were left for one week in a conditioning chamber at 25°C and 60% of relative humidity and then assessed for hydrophobicity. Specimens were chosen randomly and the water drops were set down randomly too. All the samples were cut in two tangentially and the assessed surface was the inner one. For each measurement an average of the left and the right contact angle has been made. A measure was considered as aberrant when in 5 measures in a row the average contact angle of this value was 10° up or down from others. Three series of measurements for each specimen were drawn to confirm the repetitiveness of the measurements. From these curves, the average curve was drawn to compare the effect of the impregnation on the wood (Figures 2 and 3). For each type of wood the blank sample (control) was a sample of wood impregnated with distilled water and treated in the same way. In Figure 1 it can be appreciated the positive impact of the kakishibu treatment to confer water repellency to the pine samples. All the treated specimens showed an initial contact angle of at least 90° and up to 120°. The contact angle decreased by 10°/5 min in a constant way. This slight reduction in the contact angle value does not seem to be due to water absorption in the wood surface but to water evaporation during the 5 minutes of analysis under an incandescent light. The same evaporation phenomenon has been observed on a Teflon surface by Peydecastaing *et al.* (2008) giving a similar slope in the contact angle line when the measure exceeded some seconds.

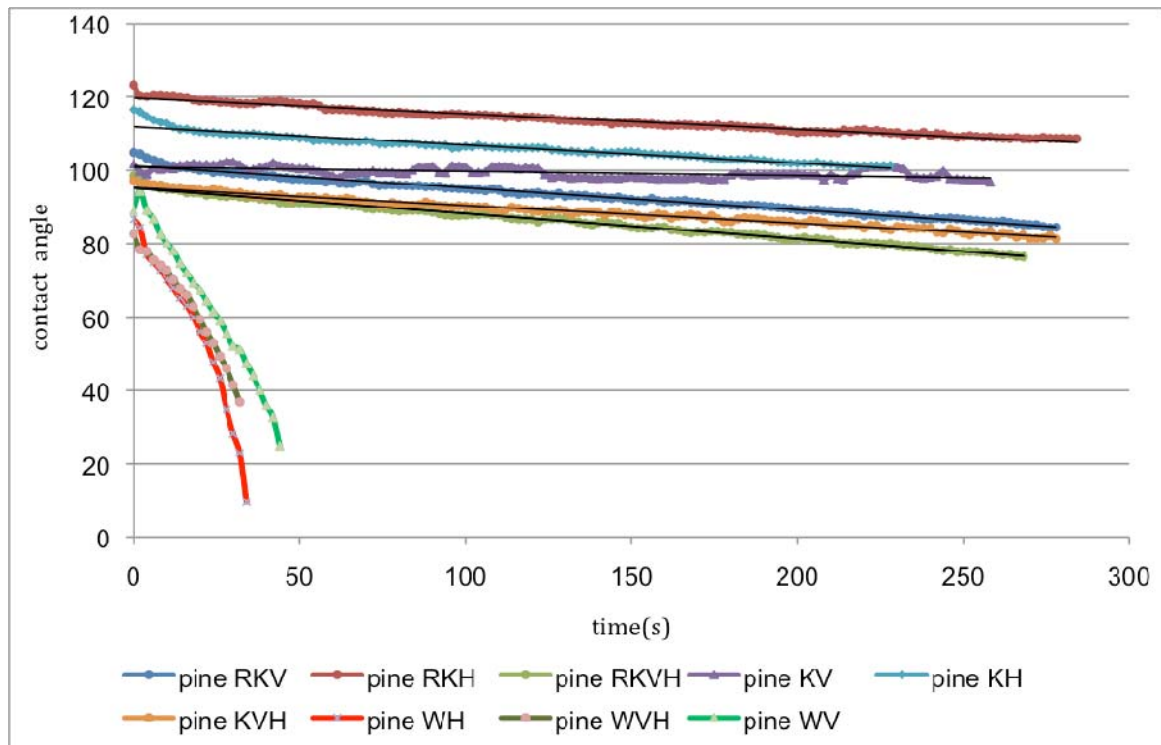


Figure 2: Contact angle of different Scots pine treated samples. K: fresh kakishibu; RK: regenerated kakishibu; V: vacuum; H: heating; W: control treated with water. Linear trends were calculated and drawn for the treated samples.

It can furthermore be observed that the samples are hydrophobic regardless of the impregnation treatment used (vacuum, heating, or both) and regardless of the type of kakishibu (regenerated or fresh). Still, the best performance was observed with regenerated kakishibu impregnated at hot temperature (RKH) followed by regenerated kakishibu impregnated with vacuum at room temperature (RKV). The blank samples treated with water showed an initial contact angle of 80 to 90° but in less than one minute the water was completely absorbed into wood. The initial high contact angle in untreated wood is probably due to surface phenomena (rugosity) but the hydrophilic nature of pine rapidly attracted the water drop. The case of beech samples is different (Figure 3). First, the water placed on the three control specimens was not absorbed but remained for more than two minutes on the assessed surface showing an initial contact angle between 60 and 70°. The samples treated with fresh kakishibu, no matter the impregnation treatment (KH, KV, and KVH) showed improved hydrophobicity (contact angles between 90 and 100°). The best values obtained for beech were lower than those for pine. Moreover, the samples treated with regenerated kakishibu had no significant effect on hydrophobicity.

This can be explained by a lack of penetrability of regenerated kakishibu into beech as shown in Figure 4. The inner section of pine sample was darker than the control one, whereas the inner section of beech samples showed no difference with the control specimen. Penetration is necessary to confer permanent hydrophobicity.

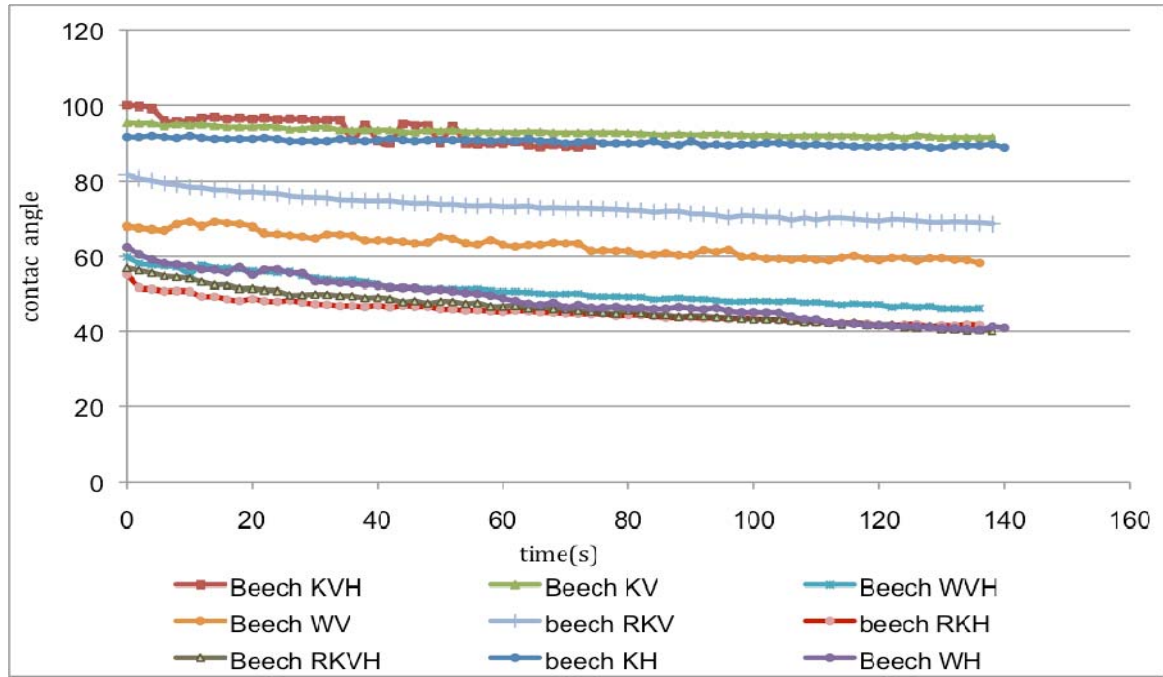


Figure 3: Contact angle of different beech treated samples. K: fresh kakishibu; RK: regenerated kakishibu; V: vaccum; H: heating; W: control treated with water.

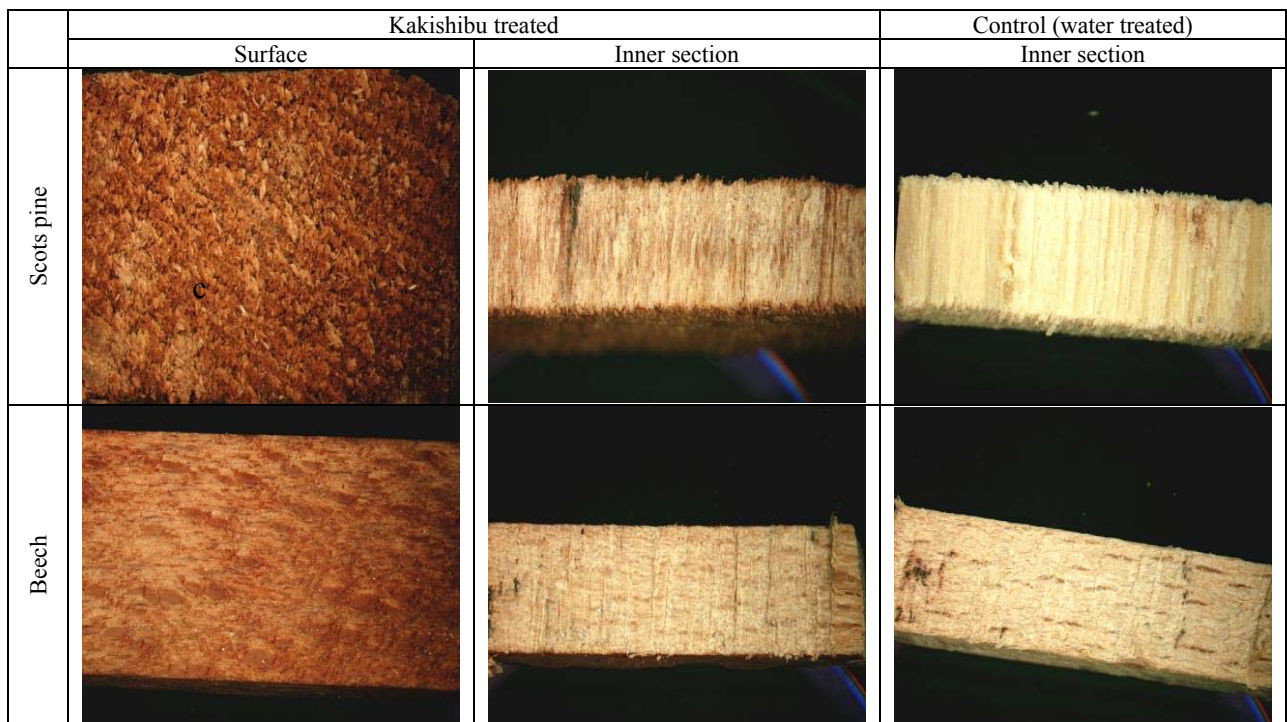


Figure 4: Aspect of the outer and inner surfaces of pine and beech samples treated with regenerated kakishibu with heating (RKH).

According to a group of Japanese researchers, Kakishibu has inhibitory effect on the growth of some species of fungi such as brown rot fungus *Tyromyces palustris* on wood (Fukuda and Kamimura 1995). It has also been used in the formulations of paintings as antibacterial agent (Kameoka 2005, Kameoka 2006). Biological resistance was assessed

by using accelerated tests on pine sapwood inspired by EN 113 for Basidiomycetes (Figure 5), EN 117 for termites, and ENV 807 for softrot (Figure 5).

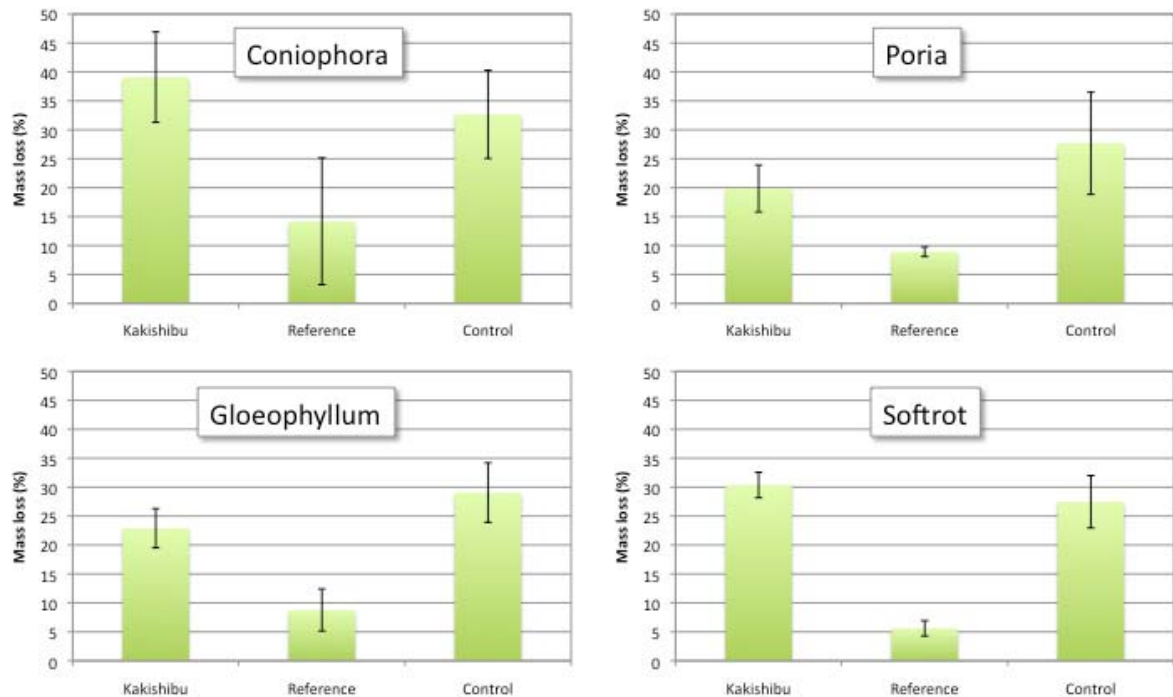


Figure 5: Corrected mass loss for samples treated with fresh kakishibu with vacuum+heating (KVH) after standard exposition to biological predators. An effective reference product was used in each case for comparison purposes. Average and standard deviations from 5 specimens.

Kakishibu offered a significant improvement in the biological resistance only in the case of *Poria placenta* and *Gloeophyllum trabeum*. In the other cases (*Coniophora puteana* and softrot decay) the mass loss was within the experimental error of the control samples. In the case of EN 117, termites survived in 80% after contact with treated samples, as well as the other group did with control samples. In both cases the degradation level was 4. Therefore, no protection was obtained against termites.

Finally, the ability to adsorb volatile organic compounds was tested with propionaldehyde. A comparison was made between sawdust treated with fresh kakishibu, with regenerated kakishibu or with water (Figure 6). The result was disappointing, as the control sample had a higher ability to trap this VOC than the kakishibu treated sawdust.

The explanation for this result can be found in the SEM photographs of treated wood samples (Figure 7). It can be observed that kakishibu clogs the diameter of numerous lumens. The available surface for adsorption is thus reduced.

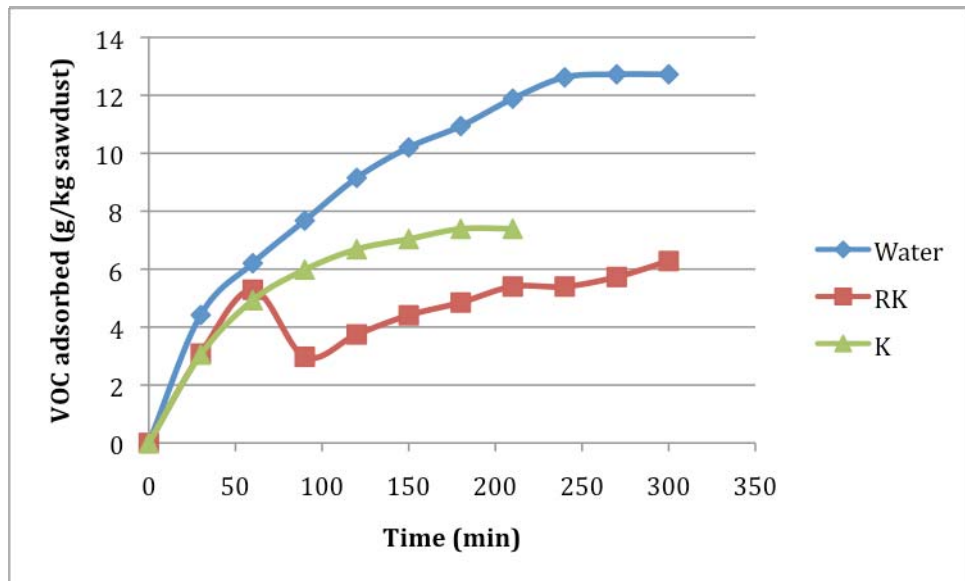


Figure 6: Mass of propionaldehyde adsorbed on sawdust treated with water, regenerated kakishibu (RK) or kakishibu (K).

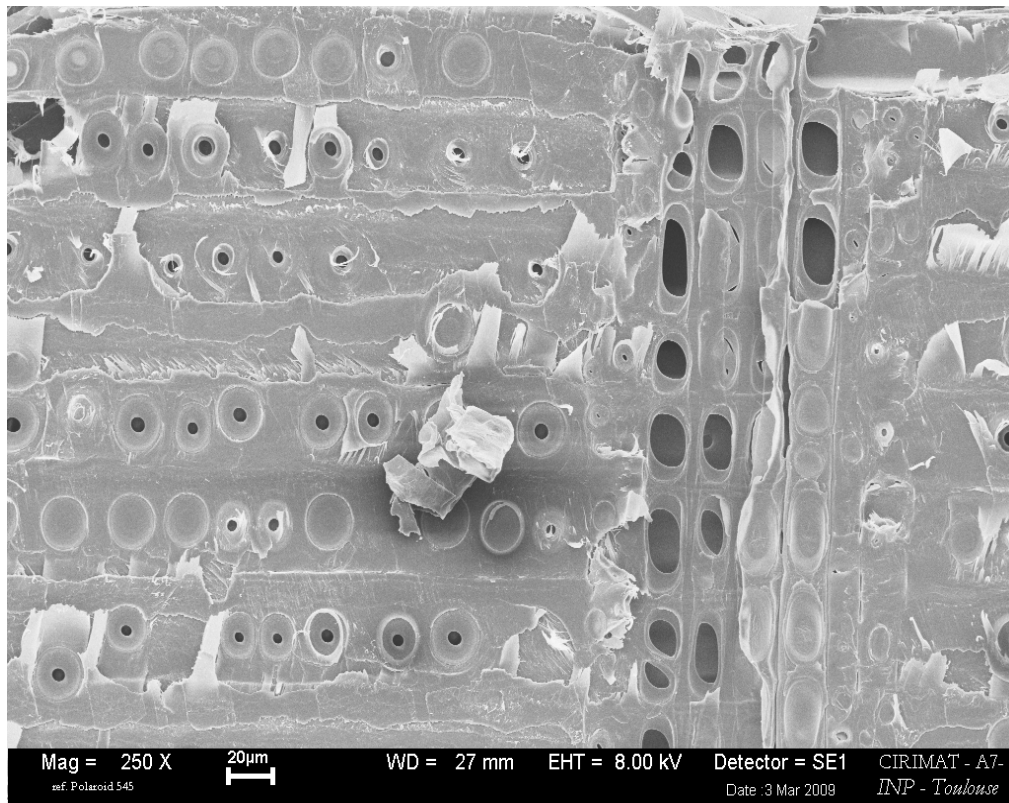


Figure 7: Scanning electron microscopy image of pine treated with fresh kakishibu with the vacuum+heating protocol.

CONCLUSIONS

This study demonstrated that Kakishibu impregnation provides a significant hydrophobic character for the inside and surface of the soft wood and for the surface of the hardwood. But we do not know what is the associated mechanism. At this point of the research concerning the effect of kakishibu on wood characteristics, we do not know how kakishibu is ab/adsorbed on wood and if there is a selective adsorption of its components. Further analysis should be done with regard to the chemical composition of kakishibu and analysis of the inside wood after impregnation. The main aim of our study was to provide some reliable proof of Kakishibu properties, because this product is often named as miracle product which is, for example, insecticide, fungicide, wood preservative, which can reinforce the wood and trap volatile organic compounds. We proved here the positive effect of Kakishibu on the water repellency of the wood. For the other assumed properties we do not have objective proofs of them. Still we need to do further investigation to assess the real impact of kakishibu on wood, especially for volatile organic compounds trapping.

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Session Seven: Panels and WPCs

Use of Chemically Modified Wood for the Production of Wood Polymer Composites (WPC) with an Optimized Property Profile

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Keywords: Wood polymer composites (WPC), chemical wood modification, compression molding, water uptake, boiling test

ABSTRACT

Solid wood from various chemical wood modification processes (commercial: thermo treatment, acetylation, furfurylation, laboratory scale: various cross-linking reactions) was milled in hammer- and knife-mills to produce particles for the use in Wood Polymer Composites (WPC). The composites of modified wood were compared to those of untreated particles of the same species; this was of importance, because different wood species were used particularly in the commercial processes. The wood particles were evaluated regarding size and geometry via mesh analysis and microscopy. The particles were compounded with polypropylene as thermoplastic matrix polymer in an extrusion process and then molded into test specimens via compression moulding. The mechanical properties were tested with regard to tensile strength, bending strength and impact bending strength. Water uptake was assessed in cold and boiling water. The use of modified wood particles resulted in an increase in dimensional stability of WPC test specimen. Water uptake was partly reduced up to 60%. The mechanical properties were significantly increased for some modified particles in dependence of the treatment without using coupling agents.

INTRODUCTION

Wood Polymer Composites (WPC) is a relatively new group of hybrid materials consisting of wood particles and thermoplastic polymers with advanced requirement specifications. Nowadays WPC products are mainly used in exterior applications such as decking or cladding elements, in automotive applications and as semi-structural elements in buildings or in non load bearing constructions (Tichy 2006, Smith and Wolcott 2006, Klyosov 2007). The aligned mixture of thermoplastic polymer(s), wood and additives, such as coupling agents and UV-stabilizers, allows an optimal use of raw materials in many applications (Hill 2000, Richter 2004, Radovanovic 2007, Grüneberg 2009). Nevertheless, several problems are observed in WPC, which are mainly related to water uptake and UV-radiation (Klyosov 2007, Gardner and Han 2009, Gnatowski 2009). Uptake of water induces dimensional changes (swelling) which results in internal stresses and deformation of the composite structure up to the collapse of the construction (Gardner and Han 2009). In addition, high moisture content supports degradation by wood decay organisms, especially by white, brown or soft rot fungi. Water uptake can be reduced in solid wood by using chemical wood modification. A basic principle of wood modification is the reduction of water uptake and an increase in dimensional stability (Hill 2006). Several processes of chemical wood modification are well known and established on the market.

MATERIALS AND METHODS

Solid wood from various processes and treatments was used. Boards of the wood were modified and chipped with classical technologies from the wood based industry. The solid wood was milled with hammer mill (VS1 N, Electra Mfg., 4mm mesh size) and a knife mill (SM1000, Retsch, 2mm mesh size) to particles. The particles were dried to ~2% moisture content before processed with a 27-mm twin screw extruder (parallel, co-rotating) to granulate. The wood-polymer ratio was 60-40% by weight. As polymer a polypropylene homopolymer was used (Sabic PP575P). The extruded granulate was used to process boards via hot pressing at 180°C (280x340x4[mm³], 4 minutes pressing time; 280x340x10[mm³] 8 minutes pressing time). 10mm thick boards were tested additionally with a raw density profile measurement device (DA-X; GreCon, Alfeld) to detect internal cracks and defects. The cold water uptake was tested in long time storage under water. The water uptake was determined by weight change over the time. The dimensional stability and the hot water uptake were determined according the standard EN1087 (2 and 5 hours boiling time). Before testing all samples were oven dried to 0% moisture content and constant weight.

RESULTS AND DISCUSSION

Long time water uptake in cold water storage

The cold water storage showed an uneven increase in the water uptake between the various treatments and wood species. Only a slight increase was observed for the acetylation treatment with *Pinus radiata* whereas the furfurylation treatment with *Fagus silvatica* showed a high increase. Except for the furfurylation treatment of *Fagus silvatica* all unmodified wood exhibit a higher water uptake compared to the modified wood of the same species. The moisture content in WPC reached constancy after 32 weeks of exposure. Independent from the speed of uptake and the wood species the untreated wood reached approximately the same moisture content. All references showed a higher uptake than the modified wood, except for furfurylated *Fagus silvatica*. The reason for that behaviour could be the formation of cracks or voids during manufacturing. The WPC produced from modified wood particles performed better than the unmodified references. Rowell (2008) describes the water uptake of WPC as a crucial and main problem. The high water uptake influences many properties of the WPC to a debased behaviour. Three main problems were reported in the literature (1) a loss in mechanical properties and (Stark 2001, Gnatowski 2009) (2) reduction of resistance against UV-radiation, temperature change, freeze-thaw cycles and (3) mechanical action (e.g. dimension change) (Bledzki *et al.* 1998, Bledzki 1998, Clemons 2002; Carlbron K. 2005). In almost all cases, more than one of these attacking mechanisms are acting at the same time and in frequent cycles or periods. Beckers *et al.* (1998) mention two ways to prevent the growth of fungi in WPC under adequate conditions of moisture and temperature; (1) treatment of wood with preservatives and (2) chemical modification of wood. The hydroxyl groups are mainly involved in the water uptake mechanism and in the enzymatic activities of fungi (rotting). If these groups are substituted, blocked or removed, for example by acetylating, the enzymatic action is disturbed and the bio-resistance of the wood is improved (Beckers *et al.* 1998, Mohebbi *et al.* 2002).

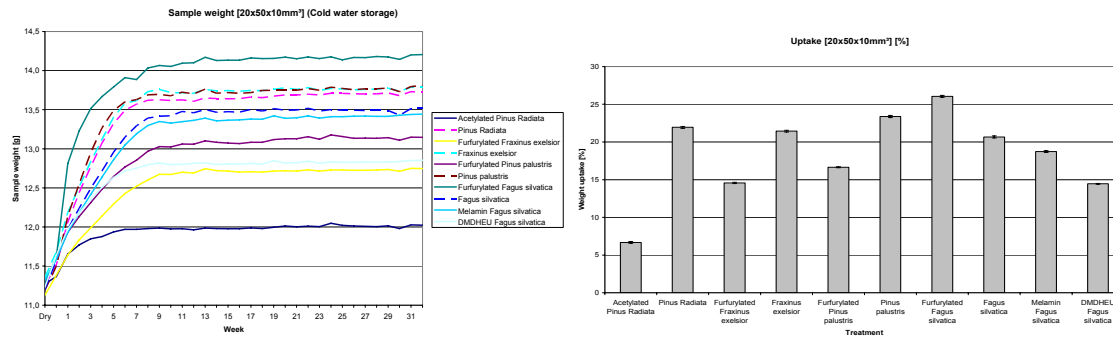


Figure 2: Increase in sample weight during cold water storage; exposure time 32 weeks.

In general the water uptake of WPC is lower compare to solid wood, by still sufficient for a biological attack by several micro organisms (Schirp et al. 2005). Considering maximum moisture content of 7% (in average) for the WPC samples using acetylated wood, a good performance against biological attacks is expected, whereas the unmodified reference WPC samples reaches approx. 23% moisture content a substantial risk of biological attack is expected. Generally, colonization of wood by mold and staining fungi requires a minimum moisture content of 20%; wood destroying fungi need higher minimum moisture content to degrade the wood ranging between 30...60% (Grosser 1985, Weiß et al. 2000, Scholz et al. 2007). A gradient of moisture can be assumed to the cross-section of the sample, were the outer area of the sample reaches a moisture content which allows biological degradation, whereas the inside of the sample remains dry.

Boiling test 2 and 5 hours according EN1087

The boiling test was performed for 2 and 5 hours. Water uptake after both exposure times showed the same trend regarding the modification of the wood fibers, whereas the 2 hours boiling test resulted in particularly higher values compare to the 5 hours test. The furfurylation showed high water uptake independent of the exposure time. High amount of water was accumulated in WPC after 2 and 5 hours boiling. Considering a polymer rich surface due to the WPC production process (Stark et al. 2004, Stark 2007) the water will predominantly enter the composite from the cut surface. The relation between "closed surface" (polymer rich area) and "open surface" (cut area) is for 10mm specimen 1.25. The form of the specimen determines the ration between volume and surface. Because of the water uptake depends on the surface area, but the amount is measured in weigth, the ratio between sample weight and surface area is calculated. Samples with a size of 50x50x10mm have ratio of 0.41g/cm². Considering these parameters and the results from long time cold water storage (other specimen size) it seems that the 10mm test specimen (boiling test) remain with a dry core section were water cannot access. Compared to the cold water storage it can be summarized that the WPC are not saturated with water neither after 2 hours as well as after 5 hours boiling.

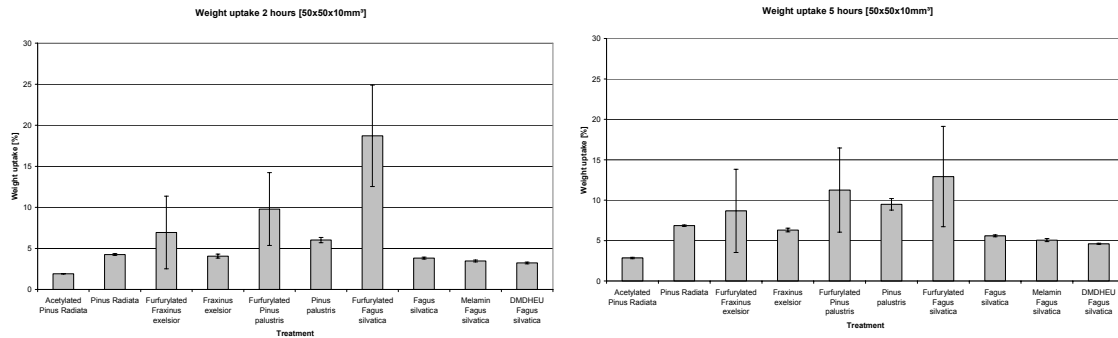


Figure 4: Water uptake of WPC samples after 2 hours exposure to boiling water (left), water uptake of WPC samples after 5 hours exposure to boiling water

The swelling in width and length of the samples after boiling in water is lower than the swelling in thickness, due to an anisotropic dispersion of the fibers. For all treatments thickness swelling reached the highest values. The references showed a slightly higher swelling than the modified samples. The significant differences in the dimensional changes were a result of the compression molding. Since compression molding, either as continuous or dis-continuous process, is well known from the wood based panel industry, using duroplastic glues instead of thermoplastics, several phenomena can be transferred to the WPC production. The speed of water uptake is different for each direction of the board (parallel or perpendicular) (Niemz 1982). Comparable to the particle board production a gentle initial press is applied to the loose WPC compound material. This step is used to increase density and strength and a collapse of wood cells (Rowell 2005).

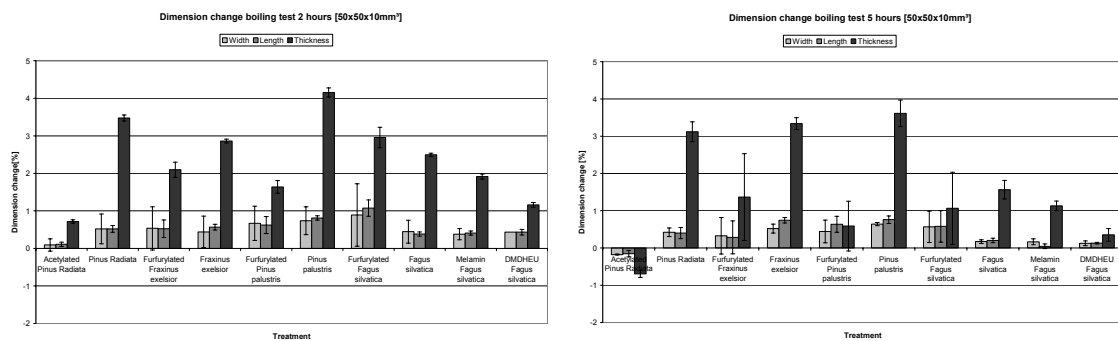


Figure 5: Dimensional change of WPC samples after 2 hours exposure to boiling water (left), water uptake of WPC samples after 5 hours exposure to boiling water

During the moisture uptake through the composite a combined thickness swelling process takes part, (1) the pure wood swelling and (2) the deformation decline (“spring-back-effect”), as part of the relaxation of compressed and collapsed wood cells due to the moisture and thermo related softening of the composite structure (Dunky & Niemz 2002). Ernst (1967) showed that 80-90% of the thickness swelling is caused by this collapsed wood cells. As higher the compression is, as higher is the spring-back-effect (Dunky & Niemz 2002). The spring-back-effect phenomena can also be observed for particle boards using a thermoplastic behavior such as PVAc (Polyvinylacetate) or EPI (Emulsion-polymer-Isocyanate; 2-component mixture) glues (Deppe et al. 2000, Dunky et al. 2002, Zeppenfeld et al. 2005). Microscopy investigations showed a remarkable orientation of the wood particles parallel to the compression surface area, compare to a random distribution perpendicular to compression surface and in the center of the sample. Stark et al. (2004) reported a similar phenomena for injection molded samples,

whereas the orientation was through the whole sample area with the direction of the melt flow.

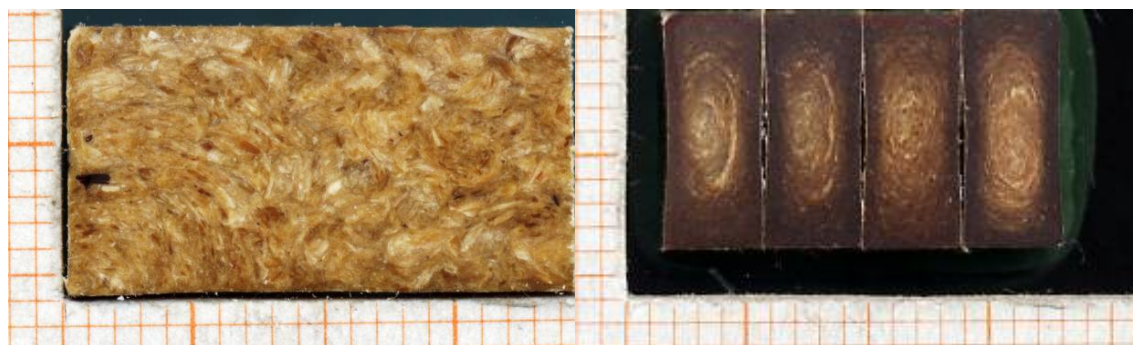


Figure 8: Cross section surface area of compressed WPC samples from compression molding with a random fiber distribution (left) and samples from injection molding with a fiber orientation in direction through the surface area (right)

Summarized, the modified wood particle showed promising results in the performed tests regarding a potential use in WPC. Further investigation will be the focus to the influence of particles size distribution in detail, the additional use of a coupling agent, the influence on durability and outside weathering.

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Enhancing the Properties of Plywood Produced by Auto-adhesion

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Keywords: Auto-adhesion, moisture resistance, plywood, self-bonding, spruce, veneer

ABSTRACT

Traditionally, plywood is produced by cross laminating wooden veneers using an adhesive to bond the veneer layers together. However, plywood can also be manufactured from rotary-cut veneers, without any additional adhesives. This is a novel, environmentally friendly, way of fabricating plywood. Several chemical bond types, *e.g.* hydrogen and covalent bonds, can be formed between veneer layers under optimal conditions. This kind of self-bonding – or auto-adhesion – of wood is more successful when the veneers are oriented parallel to one another, rather than in traditional cross-laminated plywood. However, the bonds that join the veneer layers together still suffer from poor wet strength properties. Considering densified wood, it is known that it will spring-back under humid conditions, but after certain heat treatment ‘set-recovery’ can be eliminated. Due to the nature of self-bonded plywood (in this study the compression rate circa 65%) it can be considered equal to compressed wood. Therefore, the same phenomenon can be employed here: thermal treatment of the final panel enhances wet strength, by reducing dimensional instability of the wood material. This study concentrates on 5 ply Norway spruce (*Picea abies* L.) plywood the veneer thickness of which is 3.5 mm. Part of the test panels were thermally modified so that the average loss of weight was greater than 3% whilst part remained untreated. The results of the comparison test, *i.e.* the influence of heat treatment on the quality of the bond between veneer layers is presented in this work, by examining the stability of parallel laminated, self-bonded spruce plywood during and after soaking. In summary, thermal modification had a tremendously positive effect on the stability of the bond between veneer layers.

INTRODUCTION

At present the plywood industry relies on adhesives based on fossil oil derivatives. Due to rising interest in the production of goods in a more ecological way and with a smaller carbon foot print, it is of importance to the plywood industry to consider alternative means of producing its main product – plywood. It would be preferable if such development could be performed early enough prior to a situation where supply and demand of oil no longer equate each other. According to Lambuth (1989), during earlier oil supply problems, *e.g.* wartime and oil crises, the wood products industry relied on adhesives based on renewable resources. However, this is only one solution to the substitution of fossil oil-based adhesives. During the last decade other approaches, such as self-bonded plywood have also been researched.

Cristescu (2006, 2008) as well as Okuda and Sato (2007) studied methods for manufacturing plywood without any additional adhesives. These researchers found that

higher temperatures and pressures were needed to effect adhesion compared to ordinary plywood production.

Okuda and Sato (2007) prepared adhesive free plywood from sugi veneers (MC 12.1 %). However, they were not successful with veneer alone; the bonding between the veneers was insufficient and delamination occurred. However, by utilising fine kenaf core powder (particle size of ~10 µm) as a binding agent between veneer layers they succeeded in obtaining satisfactory bonding. Nonetheless, the bonds delaminated partly in wet conditions. One of their conclusions was that high pressing temperatures “soften the solid-solid interface between particles and provide the proximity and energy required for the generation of chemical bonds”. They applied a temperature of 200°C and following pressing scheme: 5.5 MPa for 5 minutes, 3.7 MPa for 3 minutes and 1.8 MPa for 2 minutes.

In contrast to Okuda and Sato, Cristescu (2006, 2008) succeeded in producing adhesive free plywood with heat and pressure alone. The pressing temperatures applied varied from 240 to 300°C (Cristescu, 2006) and between 200 and 250°C (Cristescu, 2008) and the hot-pressing pressures varied between 4 and 6 MPa. In both these two studies constant pressure was applied and the press was closed and opened rapidly. According to Cristescu (2006), the self-bonding of veneers is more effective when the veneers are laid up parallel to one another, rather than when they are cross-laminated.

In general, plywood manufactured without adhesives (or veneers bonded with heat and pressure only) can be compared to densified wood, especially thermo-mechanical densification. Welzbacher *et al.* (2007) applied this method to Norway spruce (*Picea abies* L.) solid wood, the MC of which was between 9 and 11% utilising several press time-temperature combinations, *e.g.* compressing at 160°C for 2 and 4 hours. Furthermore, their study involved thermal treatment as well. The method used was OHT (oil-heat treatment) and the intention of the thermal treatment was to increase the dimensional stability and durability of the product. According to their results, the study was successful and thermal modification temperatures above 200°C almost completely eliminated the compression set-recovery that normally occurs in moist conditions. One set of process parameters they applied was at 200°C for 4 hours. These parameters were applied in this study as well, even though the method used was not oil-heat treatment but heat treatment under atmospheric pressure in a steam atmosphere.

The aim of this study was to investigate auto-adhesion in Norway spruce veneer and, since moist conditions can lead to debonding within the boards, study whether a post-manufacture thermal treatment could reduce or eliminate the debonding. Novel issues include self-bonded 5 ply plywood from Norway spruce as well as post-manufacture thermal treatment. This study is a part of a bigger study which considers delamination and the strength of self-bonded plywood. These issues play a key role when introducing an industrial solution for plywood produced without adhesives.

Plywood sheets were produced from rotary cut Norway spruce (*Picea abies* L.) veneer. The plywood was hot-pressed without additional glue in a laboratory press and the moisture resistance properties evaluated. Press time and veneer moisture content were varied.

EXPERIMENTAL

Wood materials

The wood material was rotary-cut 3.5 mm thick Norway spruce veneer (*Picea abies* L.) with an average dry density of 415 g/cm³. The origin of the wood is Finnish and the veneers were peeled and dried conventionally in a Finnish plywood mill. The original veneer sheets (1320×1610 mm²) were cut to size 125×590 mm². Here, the first value determines the length of the veneer, i.e. the dimension in the grain direction.

The veneers were conditioned at a temperature of 20°C and relative humidity (RH) of 65% for a minimum of 1 week, corresponding to an average equilibrium MC of 10.5%. Subsequently, the veneer thicknesses were measured in order to define the compression rate of the lay-ups (Eqn. 1).

$$rate_{compression} = \frac{thickness_{initial} - thickness_{final}}{thickness_{initial}} \quad (1)$$

A sample was taken from each piece of veneer to determine density and moisture content at the moment thickness was measured. Subsequently, half of the veneers were left to condition at RH 65% and 20°C and the other half was immersed in water for 24 hours to ensure a thorough moistening.

Press and pressing parameters

The laboratory press is an Indoor hot press the pressing dimensions of which are 800×800 mm². It was controlled by *TKK Laboratoriopuristin v1.0.3* controlling system. Three veneer lay-ups were positioned at a time into the press. Special perforated plates were placed below and above the lay-ups so as to provide exits for steam produced during pressing. A perforated plate is depicted in Figure 1.

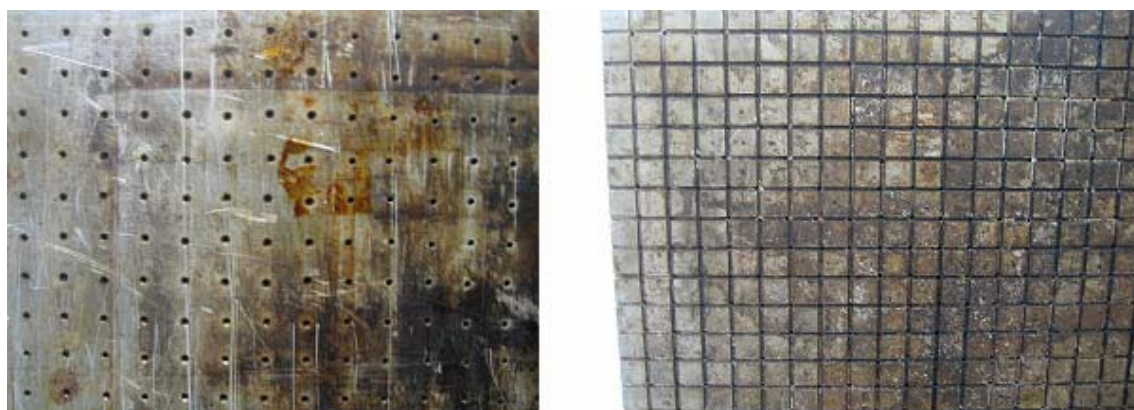


Figure 13: Photo illustrating a perforated plate above and beneath the lay-ups to provide exits for steam during hot-pressing. On the left the surface towards plywood, on the right the other side with vapour channels.

In each case the maximum pressure of 6 MPa was reached in a minute. At the end of the press cycle (either 2 or 4 hours), the pressure was lowered step by step over the last 20 minutes at 5 minutes intervals. In the first two steps the pressure was lowered by 1.5 MPa and in the remaining three steps the pressure was lowered by 1 MPa in each step. The process thus imitated the conventional plywood pressing model. By reducing the

press pressure in a stepwise manner, the internal vapour pressure within the board could be decreased controllably. To avoid thermal treatment occurring during hot-pressing, 160°C was chosen for the pressing temperature.

The plywood produced was parallel laminated but there were two lay-up types:

- Type 1 had the peeling checks hidden so that the bottom veneer had the peeling checks facing upwards and in the other veneers the checks faced downwards;
- Type 2 had all veneers with the peeling checks facing downwards.

The lay-ups were divided into groups A, B and C according to their properties. These as well as the pressing schemes are presented in Table 1.

*Table 4: Properties of lay-ups and pressing parameters. Type 1 refers to a lay-up, where the bottom veneer has the peeling checks facing upwards where as type 2 refers to a lay-up where all veneers have the peeling checks facing downwards. *Moisture content was measured same time as the thicknesses.*

Group	Condition circumstances	MC*	Lay-up type	Press conditions
A	RH 65 %, + 20°C	10.6%	Type 1	6 MPa, 160°C, 2 hours
B	RH 65 %, + 20°C	10.4%	Type 2	6 MPa, 160°C, 2 hours
C	Water immersion, + 20°C	10.2%	Type 2	6 MPa, 160°C, 4 hours

After pressing the plywood was cooled down to room temperature and conditioned for 1 week at ambient RH and 20°C. After conditioning the thickness was measured in order to define the compression rate. Subsequently the plywood sheets were sawn with a circular saw to test specimens of size 50×50 mm². During sawing the test boards were covered such a way that the plies were not ripped off from each other by the saw blade.

Thermal modification

The test specimens (50% from each group of A, B and C) were thermally modified at atmospheric pressure for 4 hours at a target temperature of 200°C. Steam was injected when the system temperature was 160°C. Steam was fed in to the system uninterrupted in such amounts that it did not condense. The loss of weight (LOW) was determined as follows (Eqn. 2):

$$LOW = \frac{mass_{oven\ dry,\ untreated} - mass_{oven\ dry,\ treated}}{mass_{oven\ dry,\ untreated}} \quad (2)$$

Moisture resistance tests

5 thermally treated and 3 untreated test specimens from each group A, B and C were oven dried for 24 hours. The thickness of the specimens was measured and the bond closure percentage was evaluated visually bond by bond. Bond closure percentage expresses the degree of integrity of two veneers next to each other. Here, 100% signifies perfect lamination whereas 0% implies total delamination. Subsequently, specimens were immersed in water. During immersion, thickness as well as bond closure percentage was measured after ½, 1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 20, 24, 30, 45, 150 hours after the immersion started.

RESULTS AND DISCUSSION

The nominal thickness of the veneers was 3.5 mm. Therefore, the nominal thickness of the 5 ply lay-up was 17.5 mm. Calculated from the measured veneer thicknesses the mean lay-up thickness was 16.99 mm and the average veneer thickness 3.40 mm. The measured plywood thickness, however, varied from 4.78 to 7.82 mm whilst the average thickness was 6.49 mm. The compression rate varied from 53.9 to 71.2%, with the average being 61.8%.

Self-bonding of the veneers was successful. Considering group specific differences, Group B provided the greatest number of specimens (practically without loss). Considering the final sawn specimens the following number of them was reached:

Group A: $n = 76$; Group B: $n = 112$; and Group C: $n = 28$. (The theoretical maximum number was 132 specimens.)

The success of group B implies that conditioning at RH 65% provides a good initial state for auto-adhesion at least for rotary cut Norway spruce veneer. Group A suffered from delamination after press opening as well as during storage. This occurred predominantly in the bottom bond. This implies that veneers should be laid up with the peeling checks facing the same direction. Furthermore, Group C suffered from problems caused by shrinkage. All veneer layers shrank noticeably during hot-pressing which led to wide cracks in each veneer layer (not necessarily in each layer within one plywood sheet). Therefore, Group C did not provide as many specimens as the other groups as continuous shrinkage during the process had prevented stable contact and thus auto-adhesion. Despite the delamination after hot-pressing, the plywood did not self-bond evenly during hot-pressing. The MC did not always decrease in a stable way and fast enough, but remained in the middle portion of the test boards causing a few (very moderate) local structural “blows” during pressing. Moreover, the centralised moisture hindered contact between the veneer surfaces leading to several unbonded spots within the fully moistened lay-ups.

With regard to heat treatment, the average LOW of 4.5% was reached whilst the minimum LOW was 3.2% and the maximum LOW 5.6%. According to Viitaniemi *et al.* (2002), compressed solid wood pieces can be stabilised by exposing them to thermal treatment at a temperature above 180°C under atmospheric pressure in a steam atmosphere. This treatment needs to last so long that the LOW is not less than 3%.

Both the untreated and heat treated plywood specimens were soaked in water and the moisture resistance of the panels was observed for the first 150 hours. The results show clearly that thermal treatment influences positively the moisture resistance of plywood produced without adhesives.

Figure 2 presents the bond closure percentage as a function of time for the bonds. Due to the mirror structure of the plywood it was assumed that the curves of the top most and bottom most bonds were alike. However, the curves differ considerably from each other. One reason for this might be that the lay-ups were set upon the hot plate and it can be said that process began pressure closure considering the bottom of lay-ups. Considering the results in general, the top most bond seem to give clearly better bond closure percentage values. There the effect of both high temperature and pressure began to

interact simultaneously. However, if the untreated specimens are not in the comparison, does the lower middle bond seem to be the best bonded. In Figures 2 and 3 the letters A, B and C refer to the group whereas “ht” refers to heat treatment and “ut” for untreated specimens.

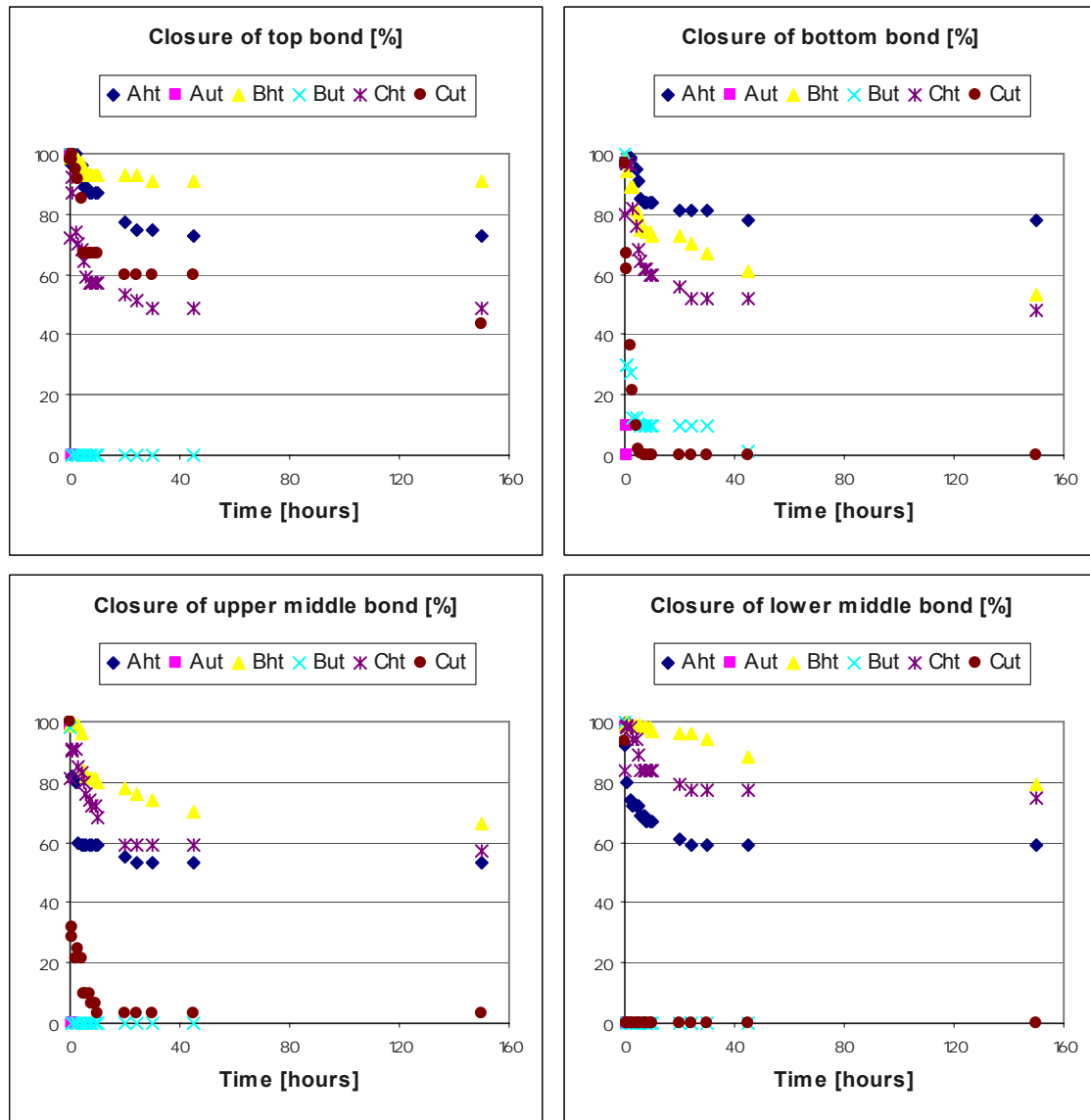


Figure 14. Bond closure percentage in 4 bonds according to their position in a lay-up. Letters A, B and C refer to the group properties of a lay-up; “ht” to heat-treated and “ut” to untreated specimens.

As Figure 2 presents the bond specific results on the bond closure percentage considering the bond position within a lay-up, does Figure 3 illustrate the average bond closure percentage as a function of time. In both Figures 2 and 3 it can easily be seen that the greatest changes due to the immersion occur during the first 5 hours and after 20 hours immersion the delamination level does not change significantly. The only exception for this was the heat-treated test sheets of Group B that showed the best moisture resistance. These bonds continued to delaminate until the end of the test. The final bond closure percentage for them was 72% after a 150 hours immersion.

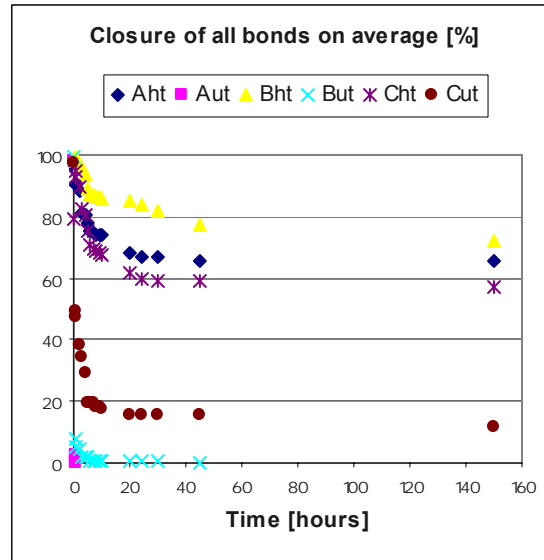


Figure 15. Bond closure percentage on average. Letters A, B and C refer to the group properties of a lay-up; “ht” to heat-treated and “ut” to untreated specimens.

Fast delamination of untreated specimens shown in Figures 2 and 3 was expected, this was most probably caused by inner stresses, in a similar manner to the way in which compressed wood behaves after compression without a certain heat-treatment (Navi and Heger 2004). Partial delamination of heat-treated specimens was most probably caused by an incomplete heat-treatment process: either relative humidity during the process was too low or the process time was too short. Here, it is possible that the specimens were not thermally modified evenly, although the LOW indicates a sufficient level of modification. The rather good results of the top bond of untreated plywood of Group C (immersed veneers) imply that some kind of heat treatment has occurred during hot-pressing due to high MC. However, this had influenced only the top most bond whereas the other bonds delaminated quickly in the immersion test.

CONCLUSIONS

The methods applied provided results partly as expected. According to the results the moisture resistance of self-bonded plywood from rotary-cut Norway spruce veneer rose remarkably after a post-manufacture heat-treatment. The untreated specimens delaminated rapidly after soaking in water. Here, the only exception was the top most bond of the fully moistened lay-up. However, even this bond could not resist the delamination for long. When the other bonds did not delaminate anymore after 45 hours immersion, this bond kept delaminating and its bond closure percentage decreased from 60% to 43% during the last 105 hours testing (the whole testing time lasted 150 hours).

Compared to the studies of Cristescu (2006, 2008) as well as Okuda and Sato (2007), considerably longer press times were chosen for both lay-up moisture types: the ones that were conditioned in RH 65%, 20°C were pressed for 2 hours and the ones that were immersed in water were pressed altogether for 4 hours. With the long press times the intention was to ensure the quality of the bonds prior to thermal modification. However, this target was not reached due to delamination occurring e.g. within the plywood sheets the bottom veneer of which was upside down compared to the other veneers in the lay-

up. According to the results it seems that it is not useful to imitate ordinary plywood this way when manufacturing self-bonded plywood.

The length of the plywood was set to 125 mm and was based inter alia on a previous study by Cristescu (2006) in which 135×135 mm² adhesive free plywood panels were manufactured. From this study, 135 mm seemed to be an appropriate length (in the grain direction) to enable water to leave the wood. This length is very significant, since most of the water within the veneers will travel longitudinally and if this distance is too great, the vapour pressure might build up in the board during manufacture leading to a premature delamination. This occurred within the lay-ups fully moistened. However, Cristescu exploited European beech (*Fagus sylvatica* L.) the MC of which was 9%. Therefore, this cannot be seen unexpected.

Despite the overall promising results the debonding of self-bonded Norway spruce plywood was not eliminated. One reason for this might be that the applied heat treatment method was not optimal. Therefore, studies will continue.

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Thermal Compression of Hybrid Poplar Wood: Cellulose Analysis

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Keywords: Wood Cellulose, hot-pressing, hybrid poplar, FT-IR and FT-Raman, GPC, XRD.

ABSTRACT

This study examines the chemical changes in the polysaccharides (cellulose and hemicellulose) of poplar wood that occur during thermal compression treatment (3.45 MPa at 150, 200 and 250°C). The changes in the cellulose structure were observed by conventional chemical methods (molecular weight by GPC) and by spectroscopic analysis (FT-IR and Raman spectroscopies). The molecular weight of cellulose was shown to decrease with temperature treatment and the degree of cellulose crystallization was also shown to change with treatment.

INTRODUCTION

Hybrid poplar species has shown promise as a viable resource for the engineered-wood based panel product industry (Peters *et al.* 2002, Kang *et al.* 2007). This is due mainly to hybrid poplar low density, high compressibility, and availability and can be a substitute for aspen in oriented strand board (OSB) panels (Roos and Brashaw 1993). One of the key steps in OSB manufacture is the hot-pressing stage. This is because, the strands are compressed and heated which promotes physical and chemical changes to occur in the wood (Paul *et al.* 2006, 2007). More specifically, wood polysaccharides (cellulose and hemicelluloses) have been shown to change upon thermal compression treatment (Boonstra *et al.* 2006). Wood polysaccharides play an important role in the mechanical properties of wood (tensile) as it related directly to the cellulose component. Also, hot-pressing has been viewed as an efficient way to upgrade the quality of wood-engineered panel like OSB through its thermal compression process. The impact of hot-pressing on the chemical and physico-chemical properties of hybrid poplar wood are therefore relevant.

The aim of this study is to determine the changes in the hybrid poplar wood polysaccharides component, namely cellulose, by using a different thermal compression treatment. The polysaccharide components were analyzed by conventional wet chemical methods (isolation of the holocellulose fraction, derivitization and Gel Permeation Chromatography (GPC)) and spectroscopic techniques (FT-IR and Raman).

EXPERIMENTAL

The hybrid poplar clone OP367 was used in this study. The logs were sliced into veneers and equilibrated to a moisture content (MC) of 8%. A portion of the veneers were vacuum dried to a MC of 0%. The veneers (150 mm x 150 mm x 1mm; 5 replicates; 0 or 8% MC) were hot-pressed at either 150, 200 or 250°C for 5 mins at 3.45MPa. The hot-pressed veneer samples were Wiley milled to pass a 2 mm screen. The ground samples were extracted with dichloromethane and the extractives free wood was then delignified using sodium chlorite to form holocellulose (Wise *et al.* 1946; Fabiyi *et al.* 2009). The holocellulose samples were used for subsequent analyses. The experimental design is a 2×3 full factorials treatment with comparisons between the control and treated samples.

Gel Permeation Chromatography (GPC): The holocellulose samples (20 mg) were derivatized to their tricarbanilate form on reaction with phenylisocyanate in pyridine at 80°C for 48 h (Suckling *et al.* 2001). The holocellulose tricarbanilate samples were dissolved in tetrahydrofuran (THF) and analysed by GPC. Separation was performed on a ViscoGEL column (I-MB HMW-3078) at 40°C on elution with THF (1.0 mL/min) using a Waters Breeze HPLC system with refractive index (Waters 2478) and triple detection (Viscotek model 270). Molecular weight calibrations were determined using a narrow polystyrene standard (99,000 g/mol) and the data was analysed using the OmniSEC v4.1 software (Viscotek).

Fourier Transform Infrared (FT-IR) Spectroscopy: FTIR spectroscopy was performed on original wood, holocelluloses and cellulose tricarbanilate samples using an Avatar 370 spectrometer (ThermoNicolet) in the attenuated total reflectance mode (SmartPerformer). Spectra were taken on 3 replicate specimens (64 scans) and the spectra averaged.

Fourier Transform (FT) Raman Spectroscopy: FT Raman spectroscopy was performed on a ThermoNicolet 960 spectrometer with excitation at 1064 nm (Nd:YAG laser, power of 200-500mW) with a spectral range of 3600 to 100 cm^{-1} . Samples were packed into glass tubes and spectra obtained from 1024 scans.

RESULTS AND DISCUSSION

The hybrid poplar wood samples were hot-pressed with two different moisture contents (0 and 8%) and three different temperatures (150, 200 and 250°C). The original wood control and hot-pressed samples were analyzed directly by spectroscopy and the molecular weight (MW) was determined on extracted and delignified samples (holocellulose).

Changes in weight average molecular weight (M_w) of the holocellulose samples by GPC as their tricarbanilate derivatives. Figure 1a shows the chromatogram of the hot-pressed (250°C, 0% MC) sample with multiple detectors and gave a M_w of approximately 300,000 g/mol. The results also showed that the weight average degree of polymerization (DP_w) of these cellulose decreased from 1000 to 700 as pressing temperature increased (Figure 1b). Microcrystalline cellulose (Whatman CF1) was used as a reference cellulose sample in the analysis and gave a DP_w of approximately 400. The control sample showed a relatively lower average DP_w value compared to other similar samples and process conditions of hardwood fiberized red maple

(Schroeder and Haigh 1979) and aspen (Laka and Chernyavskaya 2007) and suggest that the sample was not fully dissolved during the carbanilation process. The treatment reflects the decrease in average DP_w on samples. Although the average DP_w showed the trend was likely to occur when the treatment is applied to hybrid poplar wood, there is no certainty that the values are within the range since the comparison is limited.

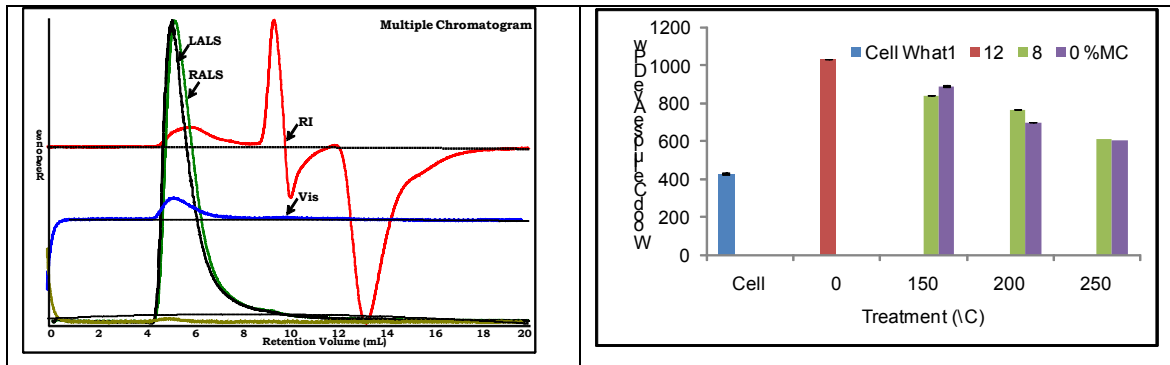


Figure 1: (A, left) GPC chromatogram of holocellulose tricarbanilate derivative from the hot-pressed poplar (0% MC at 250°C) with multiple detection (refractive index, LALLS, RALLS, differential viscometry) and (B, right) average DP_w as a result of hot-pressing treatment

FTIR spectroscopy was used to monitor changes as a result of hot-pressing poplar (Figure 2). An OH out-of-plane bending at 660 cm^{-1} , asymmetric out-of-phase ring stretch in the $C_1\text{-O-C}_4$ glucosidic bond at 898 cm^{-1} , C-O stretch at 1031 cm^{-1} , an asymmetric bridge C-O-C at 1157 and 1101 cm^{-1} , and a CH bending at 1370 and 1323 cm^{-1} were assigned to wood cellulose. The prominent shift in the spectra from 1736 cm^{-1} (carbonyl ester) to 1715 cm^{-1} (carboxylic acid) caused by hot-pressing suggests that xylan deacetylation and oxidation reactions had occurred.

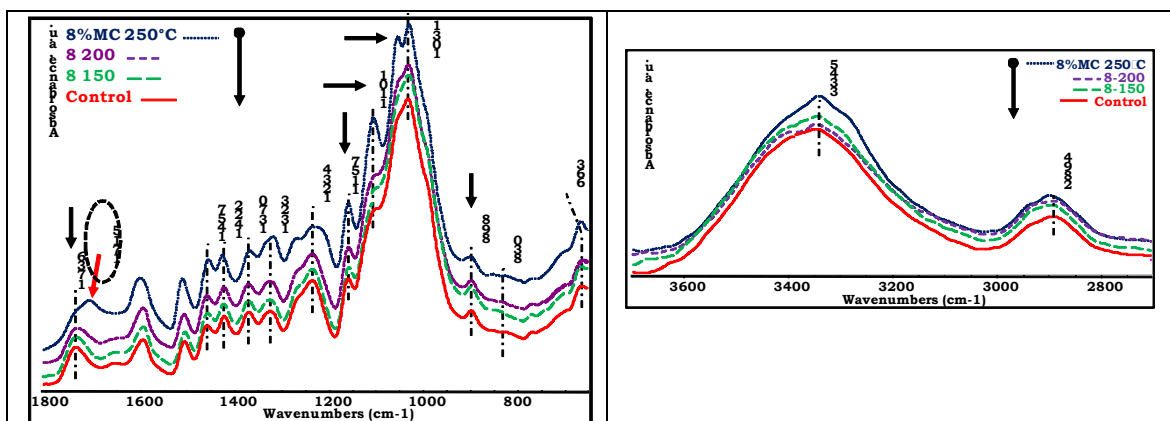


Figure 2: FTIR spectra of hot-pressed poplar (8% MC) samples showing the expanded $1800\text{-}800\text{ cm}^{-1}$ and $3600\text{-}2800\text{ cm}^{-1}$ regions

To quantify changes in the cellulose components peak fitting was performed on the spectra. The cellulose peaks at 1368 and 1315 cm^{-1} were used to determine changes in the crystalline/amorphous structure. In addition, the total relative intensity of cellulose was determined from the absorption bands at 1160 , 1323 , 1370 and 1424 cm^{-1} (Chung *et*

al. 2004) and the results are shown in Figure 3. At 250°C hot-pressing temperature a significant change in relative cellulose content (Figure 3).

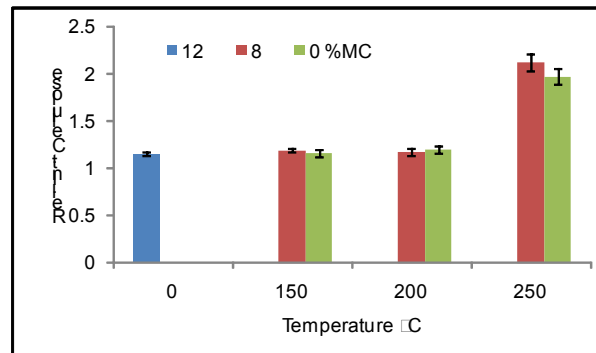


Figure 3: The average relative intensity of the specific absorption bands of cellulose for control and hot-pressed poplar samples

The carbonyl group associated with the wood polysaccharides component shows a significant difference with respect to the reference peak intensities at 1375 (C-O-C) and 1158 cm^{-1} (C-H). The relative ratio of 1734/1375 cm^{-1} decreased significantly for the hot-pressed veneers at 8% MC versus 0% MC suggesting a hydrolysis reaction (Figure 4).

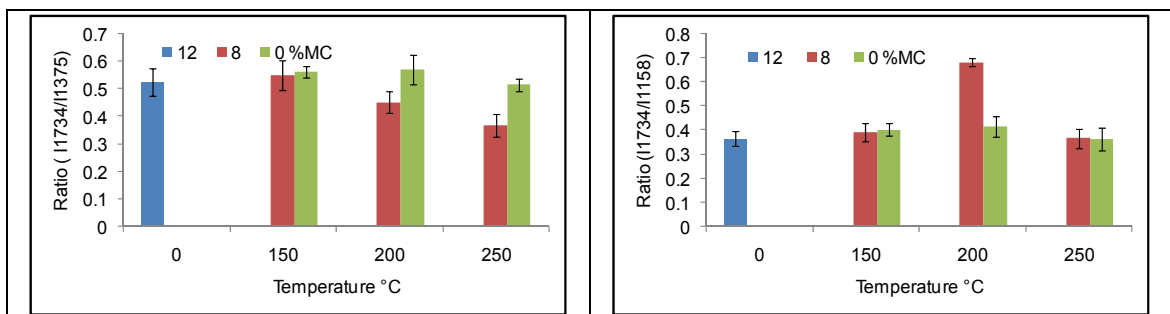


Figure 4: Changes to the carbonyl group of hot-pressed poplar samples (left, I_{1734}/I_{1375} and right I_{1734}/I_{1158} cm^{-1})

Hardwood cellulose crystallinity can be estimated from the bands at 1430, 1420, 1335 and 1315 cm^{-1} (Colom and Carrillo 2002, 2005) (Figure 5a). The band at 1422 cm^{-1} suggests a mixture of crystallize cellulose I and amorphous cellulose are present in poplar. The doublet of 1335 and 1315 cm^{-1} appears in cellulose with a higher crystalline cellulose I content. The ratio of the 1335 to 1315 cm^{-1} bands indicates an increase in crystallinity with treatment. However, these bands were not observed in the control sample. The peak at 1157 cm^{-1} represents cellulose C-O-C bridges of amorphous cellulose. Richter *et al.* (1991) determined relative changes in cellulose crystallinity from the intensity ratio (A_{1370}/A_{670}) and this approach was used to determine changes after hot-pressing (Figure 5b). The crystallinity increased significantly with pressing temperature and MC. These spectral changes have also been observed as a result of wood thermal treatment (Tanahashi *et al.* 1989, Fengel and Wegener 1989, Weimer *et al.* 1995, Bhuiyan *et al.* 2000, Yildiz and Gumuskaya 2007).

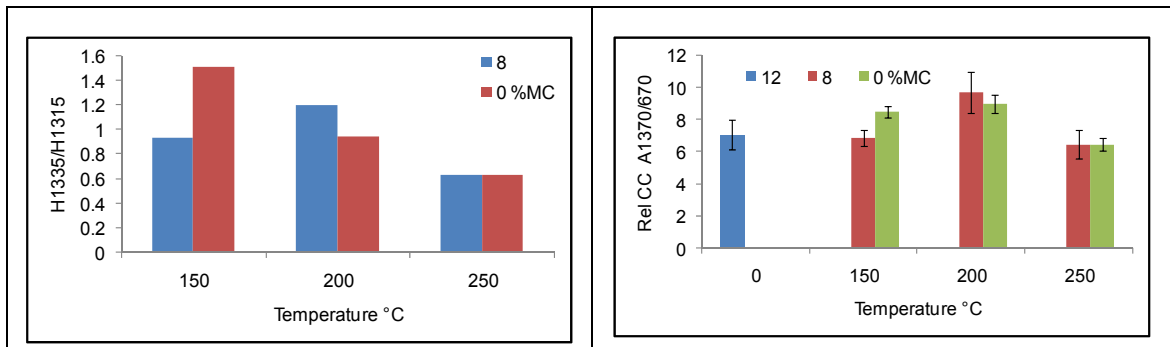


Figure 5: Amorphous cellulose and crystallized cellulose I contents (A, left) and Cellulose crystallinity (B, right) of hot-pressed poplar samples

Raman spectroscopy was also used to monitor chemical changes after hot-pressing poplar (Figure 6). The high temperature (250°C) hot-pressed samples autofluoresced, even at 1064 nm excitation and gave poor resolution spectra. The cellulose related bands were observed at 1160, 1120, 1098 and 899 cm^{-1} . Almost all cellulose bands showed changes after hot-pressing, except the peaks at 1377 and 437 cm^{-1} which were assigned to bending CH_2 and CCO stretching vibrations, respectively. The band at approximately 899 cm^{-1} is associated to antisymmetric ring stretch of amorphous cellulose.

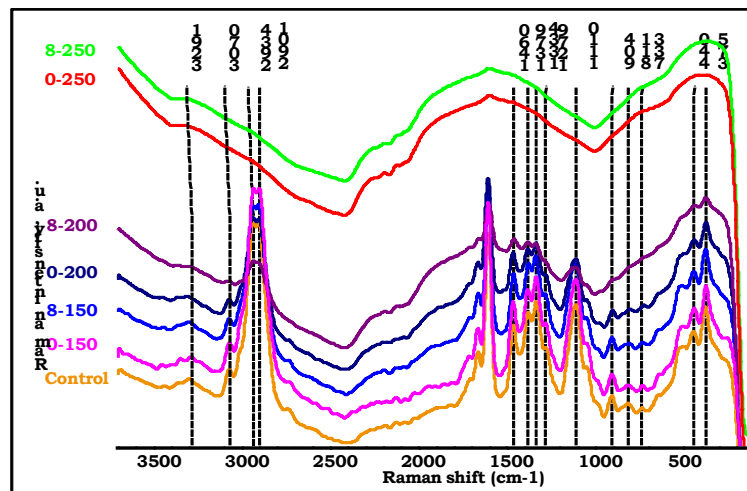


Figure 6: FT Raman spectra of hot-pressed poplar

Raman spectral peaks at 1481 and 1462 cm^{-1} are associated with crystalline (H_c) and amorphous (H_a) cellulose forms, respectively (Schenzel *et al.* 2005). The crystalline structure decreased in intensity as pressing temperature increased from 150 to 200°C showing concomitant increase in amorphous content of cellulose I (Figure 7a). Work by Agarwal (2008) used the ratio of peaks 378/1095 cm^{-1} to determine cellulose crystallinity. Using this method the crystallinity was shown to increase with pressing temperature, however MC was shown not to significant variable (Figure 7b).

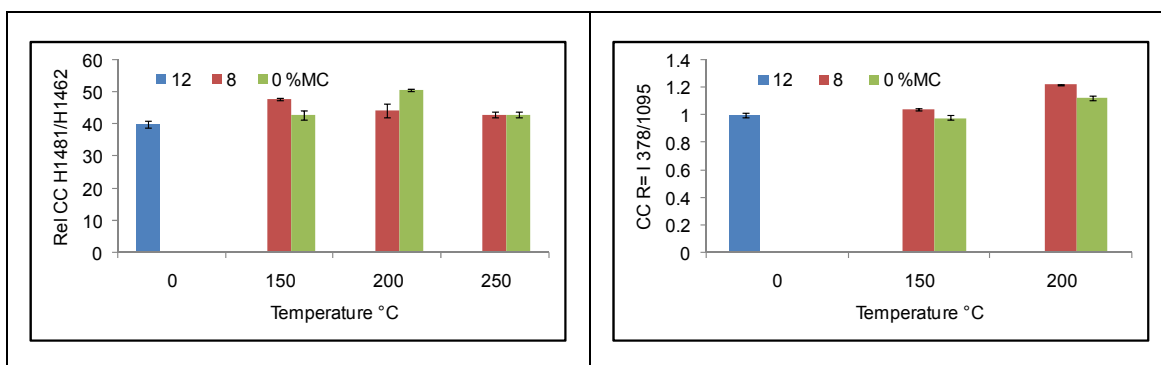


Figure 7: Intensity ratio of $1481\text{cm}^{-1} H_{\text{crystalline}}/1462\text{cm}^{-1} H_{\text{amorphous}}$ (A, left) and $R=I_{378}/I_{1095}$ (B, right) for cellulose crystallinity

CONCLUSIONS

The study shows that the hot-pressing of poplar veneers results in thermal degradation of the celulosic component of wood. In addition, the presence of moisture in the wood promotes hydrolysis reactions such as deacetylation of hemicellulose. In addition, at the higher pressing temperature (250°C) significant changes in cellulose crystallinity and molecular weight occurred. By examining the interactions between chemical changes and other wood properties (viscoelastic, mechanical, and physical) as a result of temperature and moisture optimal pressing conditions for wood consolidation, with minimal property loss, can be obtained.

ACKNOWLEDGEMENTS

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Biological Investigations of the Durability of Wood-Polymer-Composites Manufactured from Biopolymers and Acetylated Wood

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Keywords: Subterranean termites, wood-staining fungi, wood-destroying fungi, Wood-Polymer-Composites, Biopolymers

ABSTRACT

Polypropylene (PP), derived from mineral oil, currently predominates as the most important plastic used in the manufacture of wood-polymer-composites (WPC). Increasingly, in the interests of environmental protection and conservation, the polymer industries are promoting polymers which are biodegradable and derived from renewable resources. Experimental WPC-decking materials were manufactured using various blends of spruce wood flour and three biopolymers (PLA and two PLA / Co-polyester blends). Samples were tested for mechanical strength and for resistance against wood-decaying and wood-staining fungi. Performance of experimental WPC was compared against a durable wood species (Bangkirai) and with conventional WPC manufactured from PP. Conventional WPC was also manufactured using wood fibres chemically modified by acetylation. Experimental samples were challenged for 8 weeks to four types of fungi: brown rot (*Gloeophyllum trabeum*), white rot (*Trametes versicolor*), soft rot (*Chaetomium globosum*) and blue stain (*Ophiostoma piliferum*). Performance evaluation criteria were mass (weight) loss, bending strength loss (tested with a Dynstat machine) and visual assessment. Results demonstrated that, given proper composition and manufacturing conditions, WPCs made with biopolymers can be just as durable as conventional WPCs. In general, WPCs containing biopolymers reached higher final moisture contents, which leads to significant reductions in bending strength. However, WPCs manufactured with PP also experienced deterioration through biological wood decay and moisture absorption. Losses in bending strength were often attributable to gains in moisture content rather than mass losses due to fungal biodeterioration. The brown rot fungus caused the greatest mass losses in all materials. The white rot fungus had minimal effect on most materials, because spruce was used as the wood component. Specimens exposed to the soft rot fungus and the blue stain fungus experienced discoloration but no mass loss. WPCs manufactured with modified (acetylated) wood were very durable against all tested organisms imbedded against termites of the genus *Reticulitermes santonensis*.

INTRODUCTION

At the moment for the production of WPC predominantly PP, as a matrix polymer on the basis of mineral oil, is used. But through the shortage of resources and a necessary change of awareness toward the environment the population desire biological products

more than ever. In the meantime the plastics industries also distribute numerous products being biological degradable and / or consisting of renewable resources. The development of WPC based on these biological products leads to an environmentally product, which is easy to process and represent an alternative product to wood and polymer. What is missing in publications is the discussion of the biological resistance against infestation of fungi and termites as well as the effect on the mechanical properties. As most of the applications are outdoor applications this is a very important aspect for the producer and the customers. WPC were long marked as maintenance free. This is fortunately gone out of date. As WPC with polyolefins can be attacked by fungi it can be expected that this will be the same to WPC with biopolymers. But it is not clear how much these products will be attacked and how they could be protected. To get an idea some WPC-deckings with commercial biopolymers were produced for determining the biological resistance against wood-destroying and wood-staining fungi and additionally bending test were conducted. Another important topic regarding the biological durability is the resistance against termites. Termites are living in many areas around the world and causes considerable damage to wood. As WPC containing a certain amount of wood, these products are potentially at risk to be nutrition for termites. Due to these facts WPC has to be investigated regarding their resistance against termites. Since there are no standards for testing different methods were applied and evaluated regarding their efficiency.

EXPERIMENTAL

Materials

Wood

For the production of the profiles LIGNOCEL® BK 40/90 (J. Rettenmaier & Söhne) with a particle size of 300 - 500 µm was used. The wood content varied between 60 to 80 %. The acetylated wood has a WPG of 20 % (Tanczos *et al.* 2006). As reference Bangkirai and as virulence beech wood (white rot) and pine wood (brown rot, termites) were used.

Polymer

For the matrix polypropylene (PP) and three different biopolymers (Bio-Flex F1110, Bio-Flex F2110 and PLA 2002D) were used. The content varied between 18 and 40 %.

Additives

The WPC profiles based on biopolymers were made without coupling agent, because no literature was found about this topic. Furthermore the biological durability of the biopolymers in WPC should be investigated without a source of irritation. To compare the results to “Standard-WPC” profiles based on PP some profiles with different wood content and 2 % coupling agent (Scona TPPP 8112FA, Kometra GmbH) were made.

Fungi

For these tests four fungi were chosen: brown rot (*Gloeophyllum trabeum*), white rot (*Trametes versicolor*), soft rot (*Chaetomium globosum*) and blue stain (*Ophiostoma piliferum*) fungus (see Figure 16).



Figure 16: Mycelia of the four used fungi in a Petri dish. From left to right: *Gloeophyllum trabeum*, *Trametes versicolor*, *Ophiostoma piliferum*, *Chaetomium globosum*.

Termites

For these tests the termite species *Reticulitermes santonensis* De Feyteaud from SoulacsurMer, France (45°33'7" N; 1°5'37" W) was used.

Samples

Out of this the following matrix (Table 5) shows the tested materials.

Table 5: List of tested WPC samples.

Formulation	Samples														
	WPC with biopolymer									WPC with PP					
	Bio-Flex® F 1110			Bio-Flex® F 2110			PLA 2002D			Ac		U			
Wood	[%]	60	70	60	70	80	60	70	70-d	70	70	60	80	70	70
Polymer	[%]	40	30	40	30	20	40	30	30	30	28	38	18	28	30
Coupling agent	[%]	-	-	-	-	-	-	-	-	-	2	2	2	2	-
description		F1110		F2110			2002D			Ac		U			
		60/40	70/30	60/40	70/30	80/20	60/40	70/30	70/30-d	70/30	70/28	60/38	80/18	70/28	70/30

d ... dried wood Ac ... acetylated wood

The profiles, from which the samples were cut, were produced by means of extrusion. Only the pure polymer samples were made by means of injection moulding. The wood samples were prepared from a little block of wood. The extrusion was realised with a conical twin screw extruder Fibrex K38 from Cincinnati GmbH and a 4-fold gravimetric dosing system from Colortronic GmbH. The decking profile is a tool made from Greiner Extrusion GmbH (see Figure 17).



Figure 17: Geometry of the decking profile (80 x 25 mm).

The samples made with injection moulding were shouldered test bars (15 x 10/20 x 4 mm). These samples were cut to small rods (80 x 10 x 4 mm). The samples for the fungi tests and the short time termite tests were cut to 15 x 10 x d mm, the samples for the standardized termite tests (EN 117) were cut to 50 x 50 x d mm from the bottom side of the profile, which has a flat surface. The thickness "d" varied depending on the formulation of the WPC. The tests were realized with samples which showed satisfying mechanical properties after the extrusion and injection moulding. Profiles without satisfying properties had been rejected.

Methods

Mechanical test

The samples were tested regarding their bending strength before and after the exposure, water uptake and fungal resistance. It was tested by means of a Dynstat machine (see Figure 18) according to DIN 53435. The samples have to have a small dimension of (15 x 10 x d mm). The thickness “d” has to be in the range of 1.2 - 4.5 mm.

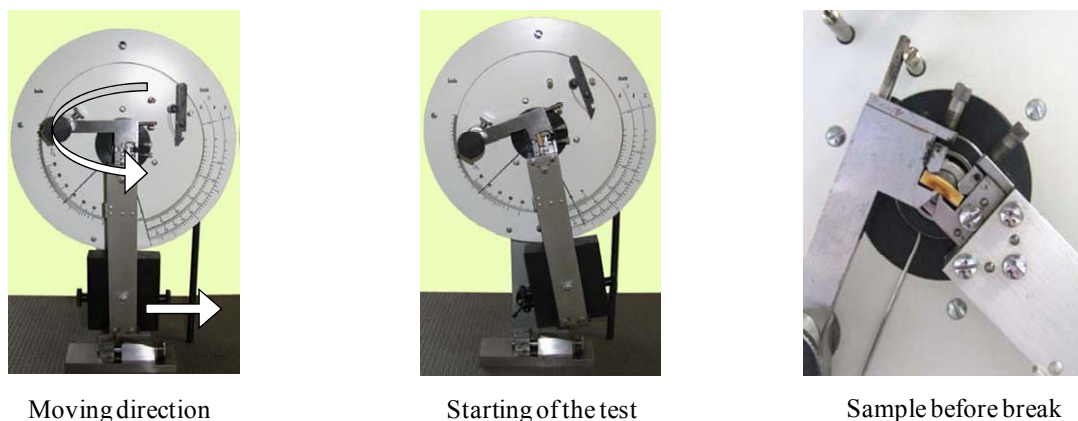


Figure 18: Dynstat machine (picture: Krackler).

Resistance against fungi

For the testing of the biological resistance against wood-destroying and wood-staining fungi the samples were cut into small pieces. Thus the duration of these tests was shortened from 16 weeks (according to ENV 12038:2002) to 8 weeks. Göhre (1955) and Retzlaff (2006) showed significant results after 3 - 4 weeks for testing of wood samples with the Dynstat machine. But due to the use of WPC materials which need more time for the water uptake the testing duration was extended. The sterilisation of the samples was made in an autoclave at 121°C for 30 minutes. After the sterilization the samples showed no changes in dimension or visual appearance. Then the samples were conditioned and arranged in a Petri dish with a culture medium of malt and agar as shown in Figure 4. As the WPC need more time for the water uptake they were placed in the Petri dishes without spacer between the sample and the culture medium. The wood samples were placed with spacer.



Figure 19: Arrangement of the samples in a Petri dish.

The incubation was done at $22 \pm 1^\circ\text{C}$ and $70 \pm 5\%$ rH (according to ENV 12038 – brown rot, white rot, and EN 152 – blue stain) and at $27 \pm 2^\circ\text{C}$ and $70 \pm 5\%$ rH (according to DIN CEN/TS 15083-2 – soft rot), respectively.

Evaluation criteria were the mass loss, the loss of bending strength and a visual assessment of the samples. The visual assessment was done for wood-staining fungi (DIN EN 152-1 – blue stain, ISO 16869 – soft rot).

Resistance against termites

To test the durability of WPC against subterranean termites three different laboratory standards were applied (Table 6 and Figure 20). The tests differ in the amount of applied termites, the test duration and the size of the specimen. The test Ebw02 was set up as screening test. The examination SAA32E09 is a test according to a TGL standard.

Table 6: Applied termite tests with specimen size, amount of termites and duration

Test	Specimen size			Test duration [weeks]	Amount of termites		
	Width [mm]	Height [mm]	Thickness [mm]		Workers	Soldiers	Nymphs
EN 117	50	50	4	8	250	2	5
SAA32E09	50	50	4	3	150	2	5
Ebw02	10	15	4	4	30	One soldier or nymph	



Figure 20: Experimental set-up: left: DIN EN 117; middle: SAA32E09; right: Ebw02.

The attack to the specimen by the termites was rated visually in four steps according to the EN 117:2005. Furthermore, the mass loss of the specimen and the mortality of the inserted termites were recorded to evaluate the tests.

RESULTS AND DISCUSSION

Before the test results regarding the effect of fungi were evaluated moisture of the WPC samples was measured. These results showed that all samples, except the WPC made with acetylated wood fibres, reached a level of moisture which enables the growing of the fungi. For the fungi *Chaetomium globosum* a moisture content of about 80 % is discussed in the literature (Unger *et al.* 2001) to be necessary. Although this moisture was not reached, the fungus shows interesting effects. The results of the samples tested without fungi showed, as expected, that the decreasing of the bending strength caused by the moisture content was increasing with increasing wood content. Almost all samples showed the highest mass lost caused by *Gloeophyllum trabeum* (brown rot), whereas *Trametes versicolor* (white rot) showed only significant mass losses at the virulence samples and the WPC based on PLA 2002D. Combined with the result from the water uptake it seems that these samples had an unsatisfactory quality of bonding.

Figure 21 show that there is no effect to the pure biopolymers as well as to Bangkirai. The results of the mass loss showed a little trend with the wood content. With the WPC

based on acetylated wood fibers the mass loss is quite low, because moisture content was not high enough for an fungus attack.

Regarding the loss of bending strength *Gloeophyllum trabeum* (brown rot) causes the highest values. This is conforming to the results of the mass loss. A bit surprising were the results of the soft rot fungus. Although this fungus caused hardly mass loss a significant loss of bending strength was determined in some cases. It can be maintained that a slight attack on a thin surface layer may cause a loss of bending strength (Huckfeldt and Schmidt 2006).

Additionally to the physical properties the samples explored to the wood-staining fungi were visually assessed complying with the standards.

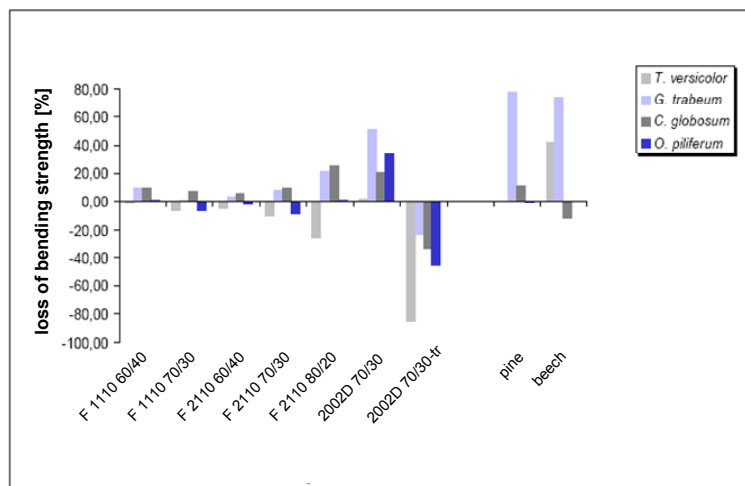


Figure 21: Loss of bending strength of WPC with biopolymer and virulence samples.

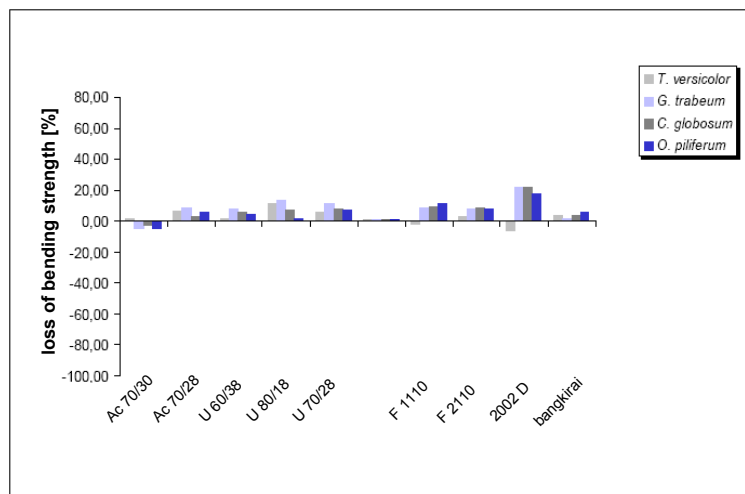


Figure 22: Loss of bending strength of WPC with PP, Bangkirai and pure biopolymers.

As shown in Table 7 the soft rot fungus causes different grades of fouling except on Bangkirai and the WPC based on acetylated wood fibers (examples in Figure 23).

The same results obtained with the blue stain fungus. All samples, except Bangkirai, WPC based on acetylated wood fibers and the pure biopolymers showed different grades of fouling.

Table 7: Visual assessments of the tested samples.

description	Samples												
	WPC with biopolymer									WPC with PP			
	Bio-Flex® F 1110		Bio-Flex® F 2110			PLA 2002D				Ac		U	
	60/40	70/30	60/40	70/30	80/20	60/40	70/30	70/30-tr	70/30	70/28	60/38	80/18	70/28
<i>Chaetomium globosum</i>	+++	+++	+++	++	++	++	+++	++	+	+	+++	+++	+++
<i>Ophiostoma piliferum</i>	1	2	1	2	2	0	1	2	0	0	1	2	1

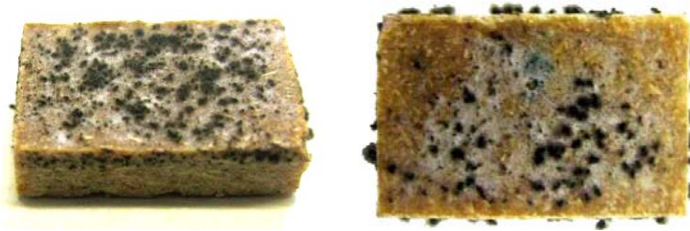


Figure 23: Samples of fouling with *Chaetomium globosum*. Left: F 1110 70/30, right: U 80/20.

The WPC based on biopolymers showed no stronger effects regarding mass loss and loss of bending strength than WPC based on PP. The pure biopolymers showed staining of the surface which has no effect on the other measured values. In these composites such slight staining may not be a significant problem, but for products with less wood fibre content this should be taken into account in dependence on the aimed application.

With the termite tests the classification of the durability is possible by analysing the visible attack. It was found that the mass loss of two samples (Figure 24 left and middle) was similar although the visible attack was significant different. Therefore only the visual assessment led to satisfying results.



Figure 24: Termite attack on different WPC: left – Ac 70/30, middle – U 70/30, right – U 80/20.

The results showed that the durability against termite attack decreases with increasing wood content, whereas the WPC based on acetylated wood showed very good

durability. The shorter test SAA32E09 (see Table 6) led to clear results and is suitable for the testing of WPC products.

CONCLUSIONS

These exploratory tests showed that considering some constraints it can be maintained that wood polymer composites based on biopolymers may have the same biological durability as so called standard WPC formulations if a good internal bonding is fulfilled. The results of the WPC with PLA 2002D were a bit surprising since these samples showed no failures at the visual check. Except the biopolymers and the WPC made with acetylated wood fibers, all samples reached a moisture level which enables a growing of three of the tested fungi. For the *Chaetomium globosum* (soft rot) the necessary moisture of about 80 % was not reached. In general only *Gloeophyllum trabeum* (brown rot) causes significant mass losses and significant losses of bending strength. *Chaetomium globosum* (soft rot) only causes little mass losses but significant losses of bending strength. At the pure biopolymers only a colouring of the surface occurred.

Considering the obtained results it can be maintained that the method, which is used for these exploratory tests, is suitable for these materials. Screening tests may be realised in a short time in lab scale with a small sample size. The chosen fungi, except the white rot fungus, were suitable for testing WPC materials. Two caused mass losses and losses of bending strength which is a mechanical problem and two fouling on the surface which is a visual problem.

As seen at the virulence samples and the different termite attacks it can be assessed, that the short time test is suitable for testing WPC products. The classification can be done in terms of visual assessment, because the determination of the mass loss led to no significant differences.

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Performance Enhancement of Wood Surfaces Used in Outdoor Applications: The Effect of Sol-gel Treatment on the Weathering Performance of Solid Wood-polymer Composites

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Keywords: colour, hardness, sol-gel, weathering, wood-polymer composites

ABSTRACT

Although wood remains the building material of choice in residential construction, it has the deleterious properties of poor durability and dimensional instability. For above-ground exterior applications such as deck flooring, important properties include hardness and weathering resistance. To improve these properties, wood was modified with acrylic polymers to slow the moisture sorption and improve its hardness and with a hybrid inorganic-organic thin film to improve its photostability. Modification of the wood was accomplished by *in situ* polymerization of acrylic monomers in the lumens and voids of the wood. Deposition of the hybrid inorganic-organic thin film in the cell walls of the outer layers of the wood was accomplished by sol-gel deposition from a water-borne sol of silsesquioxane oligomers. The weathering behaviour, including weight and colour changes of the coated and non-coated modified wood specimens under exposure to accelerated weathering conditions was performed in a Weather-Ometer™ (Atlas Material Testing Technology, LLC, Chicago, Illinois).

INTRODUCTION

Wood exposed outdoors is susceptible to degradation from sunlight, moisture, and microbial colonization. Sol-gel modification of the wood cell wall, based on surface deposition of multifunctional alkoxy silanes, has been shown to improve moisture resistance and photostability of wood substrates (Tshabalala *et al.* 2003a, 2003b, Tshabalala *et al.* 2007). Evans (2009) has observed (that modification technologies designed to impart photostability to wood are most likely to be successful when used as surface treatments.

In situ polymerization of monomers (such as acrylates and methacrylates) in the voids or lumens of solid wood can produce a water resistant and harder material. It does not make the wood dimensionally stable, but can improve resistance of the wood to water sorption by filling the voids with polymer and impeding moisture movement.

Various acrylic monomers have been evaluated for dimensional stability, ability to exclude water vapor and liquid water, and hardness (Ellis and O'Dell 1999, Ibach and Ellis 2005). Different combinations of hexanediol diacrylate (HDDA), hydroxyethyl methacrylate (HEMA), hexamethylene diisocyanate (Desmodur N75, DesN75), and maleic anhydride (MAN) were polymerized *in situ* in solid pine, maple, and oak wood. The rate of water vapor and liquid water absorption was slowed, and the rate of swelling was less than that of unmodified wood specimens, but the dimensional stability was not permanent (Ellis and O'Dell 1999).

Crosslinking agents are generally used to increase reaction rate and improve the physical properties of wood-polymer composites (WPCs) (Kenaga 1970). Some of the crosslinking agents frequently used with methyl methacrylate (MMA), styrene, or other vinyl monomers are trimethylolpropane triacrylate, trivinyl isocyanurate, trimethylolpropane trimethacrylate, ethylene glycol dimethacrylate, trimethylene glycol dimethacrylate, tetraethylene glycol dimethacrylate, polyethylene glycol dimethacrylate, and divinylbenzene. WPCs with only MMA show a void space at the interface between cell wall and polymer (Kawakami *et al.* 1977). With addition of crosslinking esters such as di- and tri-methacrylate, the shrinkage (and hence void spaces) of the polymer during polymerization increases. On the other hand, in the WPCs containing polar esters having hydroxyethyl and glycidyl groups, the voids caused by the shrinkage of polymer were found to form inside the polymer itself, suggesting better adhesion of the polymer to the inner surface of cell wall (Kawakami *et al.* 1981).

WPCs made with birch and pine and impregnated with MMA or styrene-acrylonitrile were more resistant to surface checking than untreated wood when exposed to accelerated weathering in a Weather-Ometer™ (Atlas Material Testing Technology, LLC, Chicago, Illinois) for 1,000 h (Desai and Juneja 1972). The styrene-acrylonitrile treatment performed better than MMA. A combination of cell wall-modifying treatments (butylene oxide or methyl isocyanate) with MMA lumen-filled treatments showed improved resistance to the degradative effects of accelerated weathering in a Weather-Ometer™. The use of MMA in addition to the cell wall-modifying chemical treatments provides added dimensional stability and lignin stabilization and has a significant effect on weatherability (Rowell *et al.* 1981).

The objective of this study was to explore the effect of hybrid inorganic-organic sol-gel deposits on weathering properties of solid wood-polymer composites.

EXPERIMENTAL

Materials and Methods

Wood specimens were prepared from western red cedar (*Thuja plicata*) boards in the form of wafers, 51.3 mm × 0.8 mm × 15.8 mm (longitudinal, tangential and radial directions). The specimens were placed in a controlled humidity room to condition at 65% relative humidity (RH), 26.7 °C to a constant weight before coating.

Concentrated sols of water-borne silsesquioxane oligomers, WSA-9911, WSA-7021 and WSA-6511, containing aminopropyl, aminoethylaminopropyl and aminopropyl, vinyl functional groups, respectively, were purchased from Gelest, Morrisville, Pennsylvania. Sols for coating the wood specimens were prepared in separate containers by diluting one part by volume of each concentrated sol with 63 parts by volume of deionized water to yield nominal weight percentage contents of 1.66 for WSA-9911, 1.72 for WSA-7021, and 1.73 for WSA-6511. This dilution afforded the longest time before onset of gelation. Hexanediol dimethacrylate (HDDMA) was from Sartomer Company, West Chester, Pennsylvania. Trimethylolpropane trimethacrylate (TMPTM) was from Aldrich Chemical Company, Milwaukee, Wisconsin. 2,2'-azobis(2-methylbutanenitrile) (VAZO 67G), was from DuPont Specialty Chemicals, Wilmington, Delaware.

Specimens were divided into 18 treatment groups as summarized in Table 1. Each treatment group, except P and PWC, consisted of five replicates.

In situ, void filling polymerization

The wood specimens were dried at 105°C for 24 h to remove moisture and then weighed. The wood specimens were placed in a glass crystallizing dish and weighted down with glass weights to hold them under the solution. A vacuum (0.7 to 1.3kPa) was applied to the wood for 30 min. The monomer solution containing HDDMA, 0.5% VAZO 67G catalyst, and 5% TMPTM (if added) crosslinker was introduced into the container. The vacuum was maintained for 5–10 min to remove air from the monomer. The vacuum was then released, and the chamber returned to atmospheric conditions. The wood and solution were allowed to stand for 30 min. The treated wood was removed from the solution, wiped to remove excess chemical from the outside of the specimens, wrapped in aluminum foil, placed in a hot oven, and heated at 105 °C for 20 h. Aluminum foil was then removed, specimens were weighed again, and percentage weight gain calculated. Some polymer was on the surface of the wood and was left on.

Surface modification

The treatments are described below in Table 1. Each group of specimens was coated by placing in separate reaction vials filled with 40-mL of the appropriate WSA sol. The reaction vials were then placed on a horizontal shaker to react for 24 h at room temperature. After reaction, the specimens were placed in an oven to dry for 6 h at 65° C, and to cure for 24 h at 105°C.

Table 1: Description of surface treatment specimens

Specimen ID	Treatment	Replicates
C	Control	5
P	Void filling polymerization	10
PWC	Void filling polymerization w/crosslinker	10
W6	WSA-6511	5
W6+P	WSA-6511 followed by void filling polymerization	5
W6+PWC	WSA-6511 followed by void filling polymerization w/crosslinker	5
P+W6	Void filling polymerization followed WSA-6511	5
PWC+W6	Void filling polymer w/crosslinker followed by WSA-6511	5
W7	WSA-7021	5
W7+P	WSA-7021 followed by void filling polymerization	5
W7+PWC	WSA-7021 followed by void filling polymerization w/crosslinker	5
P+W7	Void filling polymerization followed by WSA-7021	5
PWC+W7	Void filling polymer w/crosslinker followed by WSA-7021	5
W9	WSA-9911	5
W9+P	WSA-9911 followed by void filling polymerization	5
W9+PWC	WSA-9911 followed by void filling polymerization w/crosslinker	5
P+W9	Void filling polymerization followed by WSA-9911	5
PWC+W9	Void filling polymer w/crosslinker followed by WSA-9911	5

Accelerated weathering

For accelerated weathering studies, three replicates from each treatment group were exposed for a total of 240 h in a Ci-65 Weather-Ometer™ (Atlas Material Testing Systems, Chicago, Illinois) using Program 1, which consisted of a 2-h cycle (102 min UV radiation only followed by 18-min radiation and water spray at a rate of 0.2 L/min). The light source was a Xenon arc lamp with borosilicate inner and outer filters, and its irradiance was controlled at 0.35 W.m⁻² at 340 nm. During the light and spray cycle, the black panel temperature (BPT) was 50±5 °C; and RH was 80±5%.

Colour measurements

The colour of each specimen was measured at three contiguous spots with a Konica Minolta CR-400 Chroma Meter (Minolta Co., Ltd., Osaka, Japan).

Colour measurements were determined according the CIE L*a*b* system of three parameters. The L* axis represents the lightness and varies from 100 (white) to zero (black). The a* coordinates represent chromaticity with +a* for red and -a* for green; and the b* coordinates represent chromaticity with +b* for yellow and -b* for blue. L*, a* and b* were measured before and after 240 h exposure in the Weather-Ometer™. These values were used to calculate the resulting colour change, ΔE*, and chromaticity change, ΔC* according to the following equations:

$$\Delta L^* = L^*_{(t)} - L^*_{(i)} \quad (1)$$

$$\Delta a^* = a^*_{(t)} - a^*_{(i)} \quad (2)$$

$$\Delta b^* = b^*_{(t)} - b^*_{(i)} \quad (3)$$

$$\Delta C^* = \{\Delta a^{*2} + \Delta b^{*2}\}^{1/2} \quad (4)$$

$$\Delta E^* = \{\Delta L^{*2} + \Delta a^{*2} + \Delta b^{*2}\}^{1/2} \quad (5)$$

ΔL*, Δa*, and Δb* are differences between the initial (i) and exposure time (t) values.

RESULTS AND DISCUSSION

The average weight percentage gain and standard deviations of the *in situ* polymerized specimens are summarized in Table 2.

Table 2: Average weight gain of specimens after in situ polymerization

Specimen ID	Treatment	WPG (STDEV)
P	Void filling polymerization	68.31 (9.84)
PWC	Void filling polymerization w/crosslinker	63.82 (8.79)
W6+P	WSA-6511 followed by void filling polymerization	64.95 (6.73)
W6+PWC	WSA-6511 followed by void filling polymerization w/crosslinker	57.39 (3.58)
W7+P	WSA-7021 followed by void filling polymerization	72.94 (3.54)
W7+PWC	WSA-7021 followed by void filling polymerization w/crosslinker	67.15 (7.09)
W9+P	WSA-9911 followed by void filling polymerization	68.63 (4.37)
W9+PWC	WSA-9911 followed by void filling polymerization w/crosslinker	59.62 (7.83)

The specimens were evaluated for weight loss and colour changes caused by weathering.

Weight loss

As shown in Figure 1, specimens treated with either the polymer or with polymer with crosslinker or with sol-gel showed less weight loss compared to the non-treated control specimens. This suggests that the polymer or the sol-gel or a combination of both the polymer and the sol-gel improved the resistance of the wood to erosion under accelerated weathering conditions. Improved resistance to erosion increased in the order sol-gel < polymer \approx polymer with crosslinker < sol-gel with polymer \approx sol-gel with polymer+crosslinker.

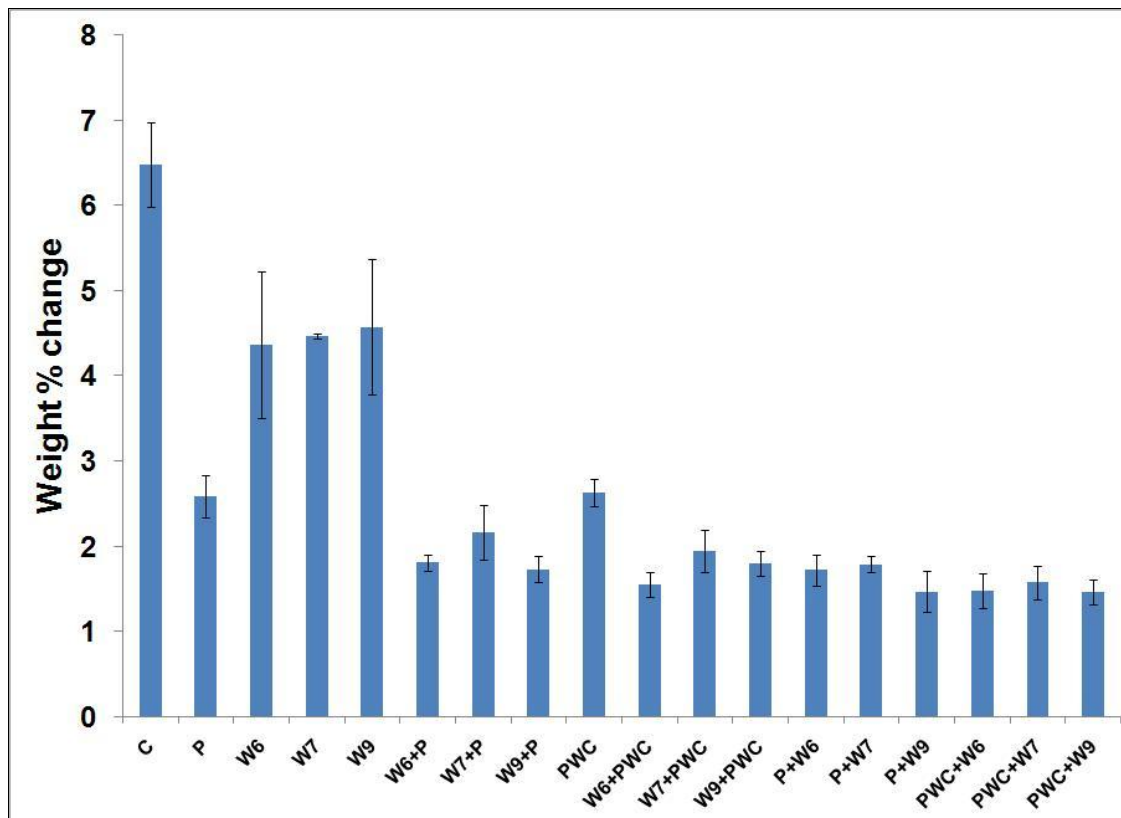


Figure 1: Average weight percentage change of specimens after 240-h exposure in Weather-Ometer™

Colour change measurements

Figure 2 shows the average lightness change, ΔL^* of the specimens after exposure for 240 h in the Weather-Ometer™. Except for those specimens treated with the sol-gel followed by polymer with crosslinker, there was little difference in lightness change between the treated and the control non-treated specimens. However, compared with control non-treated specimens, average chromaticity changes, ΔC^* , were generally lower for those specimens treated with sol-gel, WSA6511 in combination with either the polymer or polymer with crosslinker. (See Figure 3).

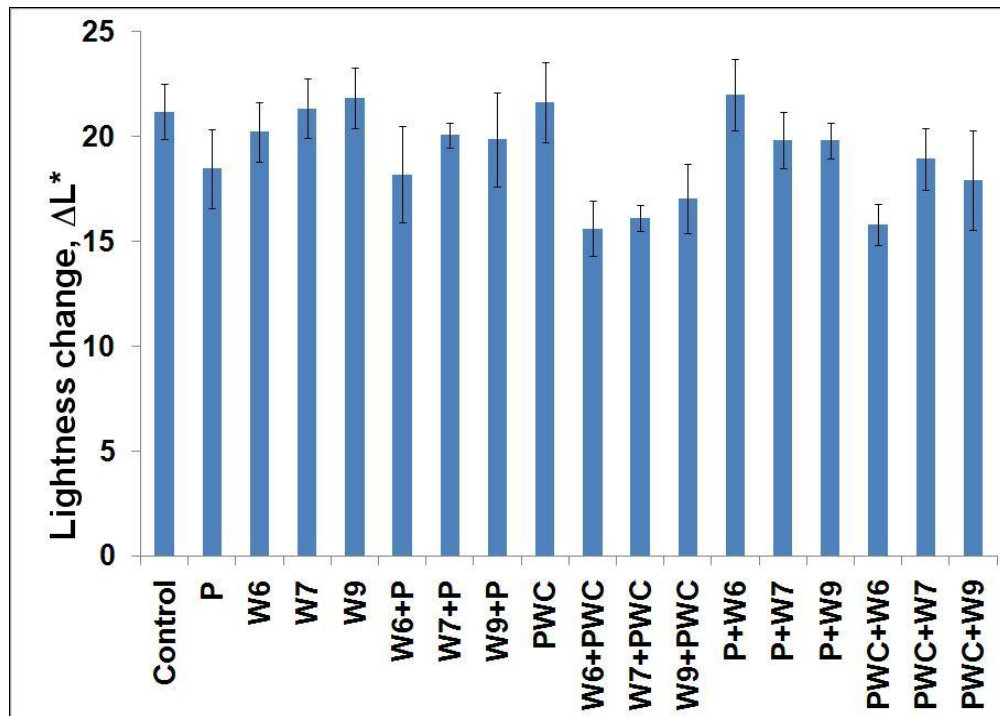


Figure 2: Average lightness changes of specimens after 240-h exposure in Weather-Ometer™

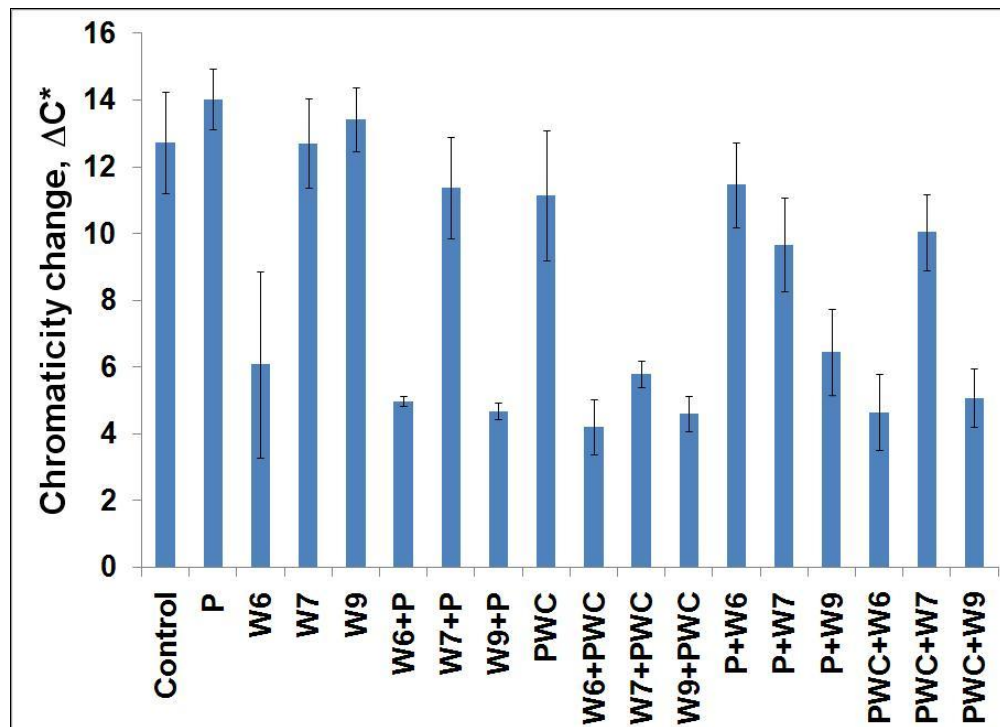


Figure 3: Average chromaticity changes of specimens after 240-h exposure in Weather-Ometer™

Average colour changes of the specimens after 240-h exposure in the Weather-Ometer™ are shown in Figure 4. Specimens treated with sol-gel followed by polymer with crosslinker showed the greatest resistance to colour change compared with the non-treated control specimens. It is also interesting to note that the average colour changes, ΔE^* , followed a similar pattern to the average lightness changes as illustrated in the plot of ΔE^* versus ΔL^* in Figure 5.

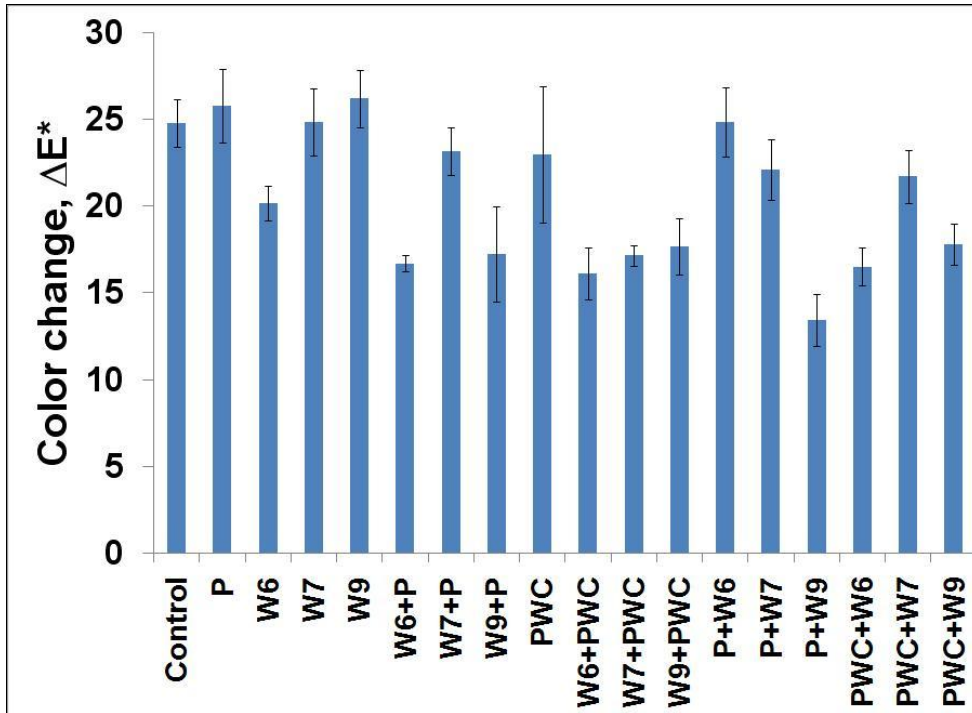


Figure 4: Average colour changes of specimens after 240-h exposure in Weather-Ometer™

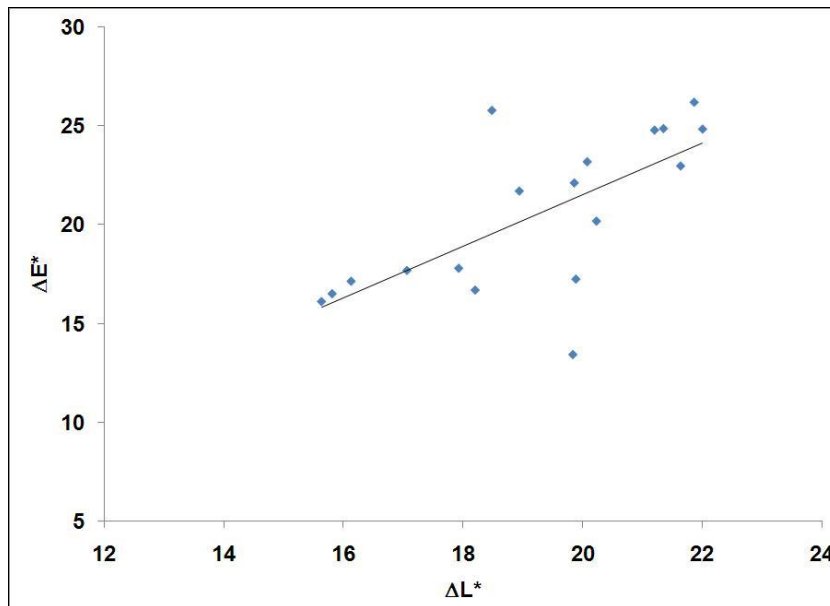


Figure 5 Plot of ΔE^* versus ΔL^* , with trend line indicating a linear correlation between these two parameters

CONCLUSIONS

These results indicate that some sol-gel systems (for example WSA6511) have the potential to improve colour stability of wood-polymer composites. In addition, the order of treatment appeared to be important. For example, specimens that were treated with sol-gels before *in situ* polymerization with polymer or with polymer and crosslinker appeared to show better resistance to weathering in terms of resistance to weight loss and colour stability.

Weathering exposure on these specimens continues. Future research is required to optimize the sol-gel deposition conditions in addition to understanding the influence of the chemistry of the sol-gel systems on weathering performance of wood polymer composites.

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**Session Eight:
Weathering, Surface Properties
and Marine Borers**

Wood Veneer Modification by Atmospheric Pressure Plasma Treatment for Improved Absorption Characteristics

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Keywords: Plasma, wood, soaking, immersion, contact angle, impregnation, DBD

ABSTRACT

Most methods in current use for wood modification are based on impregnation by liquid systems carrying the modifying agent. The limiting factor in the impregnation processes is the rate of liquid penetration into the wood. Increasing the penetration rate would decrease operating time and production costs. Plasma treatment of wood is known to increase surface polarity and hydrophilicity, which should facilitate penetration into the wood and absorption of the water-borne impregnation agents. In this study, the effect of plasma treatment by a dielectric barrier discharge (DBD) at atmospheric pressure on the absorption characteristic of wood veneers was investigated. It was found that the absorption characteristics of hardwood veneers were significantly improved by the plasma treatment.

INTRODUCTION

Impregnation of wood is a common method to improve properties such as durability and dimensional stability. Common impregnation processes include brush and spray treatment, dipping, steeping and high-pressure vacuum processes using conventional liquid impregnation agents, which include paints, lacquers, innovative wood modifiers such as DMDHEU (1,3-dimethylol-4,5-dihydroxyethylene urea) and melamine (Kabir *et al.* 1992, Militz 1993, Yusuf 1996, Brich and Kozhin 2001, Gindl and Gupta 2002, Hill 2006, Shukla and Kamdem 2010). These processes can be impeded by insufficient soaking of the wood, which requires lengthy process times, and poor ability to absorb the modifying agent, resulting in inefficient impregnation. Plasma treatment is known to enhance the wetting characteristics of materials that include plastic, metal, glass and wood (Inagaki 1996, Hippler *et al.* 2001, Rehn *et al.* 2003). Studies using contact angle measurements and XPS (X-ray photoelectron spectroscopy) analysis to determine the characteristics of plasma-treated surfaces of wood and WPC (wood/plastic composite) revealed a significant increase of polar groups on the surface, resulting in increased surface energy (Klarhöfer *et al.* 2005, Wolkenhauer *et al.* 2007a, Avramidis *et al.* 2009). Wolkenhauer *et al.* (2007b) and Avramidis *et al.* (2010) showed that curing of PVAc (polyvinyl acetate)-glued fibre boards, particle boards and hardwood veneers can be accelerated significantly by plasma treatment. The increased surface polarity of the plasma-treated wood surfaces positively affects the penetration of polar liquids into the bulk material (Wolkenhauer *et al.* 2007b). Furthermore, Jamali and Evans (2010) reported surface etching including etching of pits and bordered pits, improving

penetration by low-pressure plasma treatment. Similar etching effects were found on the surfaces of atmospheric pressure plasma-treated WPC (Wolkenhauer *et al.* 2008) and are likely to occur also for atmospheric pressure plasma-treated wood surfaces. Immersion tests were done as well as water contact angle measurements to assess surface characteristics and treatment effectiveness in order to assess the water uptake of untreated and atmospheric pressure plasma-treated veneers of several wood species (oak, beech, spruce, pine). Additionally, the soaking ability of plasma-treated beech and oak veneers was tested with DMDHEU and melamine.

EXPERIMENTAL

Materials

Sliced veneers ($55 \times 40 \times 0.6 \text{ mm}^3$) of oak (*Quercus* sp.), beech (*Fagus sylvatica*), spruce (*Picea abies*) and pine (*Pinus sylvestris*) were stored at 20°C and 65% RH before testing.

Water uptake and WPG

Water uptake (the soaking ability) of the samples was determined by a simple immersion test at atmospheric pressure and a temperature of 20°C. The immersion durations were 1 s, 5 s, 10 s and 60 s. The samples were weighed before and after immersion in water and the percentage increase in mass (water uptake) was calculated by Equation 1:

$$\text{Water uptake} = ((M_2 - M_1)/M_1) \times 100 \% \quad (1)$$

where M_1 is the mass before immersion and M_2 is the mass after immersion.

To determine the solids content of impregnation agents after impregnation with melamine solution and DMDHEU solution, the WPG (weight percentage gain) was calculated using Equation 2:

$$\text{WPG} = ((M_m - M_u)/M_u) \times 100 \% \quad (2)$$

where M_m is the weight of the oven-dried immersed samples and M_u is the weight of the oven-dried untreated samples

Water Contact Angle (WCA)

In order to assess surface properties, water contact angles were determined for untreated and plasma-treated surfaces using the Krüss GS 10 (Hamburg, Germany) contact angle measuring system and the corresponding Krüss DSA 1 software. Contact angle measurements were done by the static sessile drop method. Nine droplets (3 droplets/sample) with a volume of 10 μl were measured for each parameter. The contact angle was determined at 1.0 s after impact of the water droplet on the surface. The contact angle measurements were done directly after the plasma treatment.

Plasma Setup

Figure 1 shows a sketch of the DBD (dielectric barrier discharge) setup. The samples were positioned centrally between two insulated electrodes ($300 \times 50 \times 50 \text{ mm}^3$) so that the discharge gap between the sample and the electrodes was 2 mm on each side. An alternating high-voltage ($u \approx 35 \text{ kV}$ peak) pulse generator with a pulse duration of 2 μs and a pulse repetition frequency of 17 kHz was connected to one electrode (bronze,

dielectric: Al_2O_3 , thickness 6 mm) and the other electrode (aluminium, dielectric glass, thickness 4 mm) was grounded. In this unsealed setup, ambient air at room temperature was blown through the discharge gaps at a velocity of $\approx 4\text{m/s}$. To minimize thermal influence, a treatment duration (t_D) of $t_D = 1\text{ s}$ was followed by a break of 1 s for $t_D > 1\text{ s}$ (Wolkenhauer *et al.* 2009). The gas temperature during the treatment was $< 50^\circ\text{C}$ as measured with a fibre optic thermometer (FTI-10, FISO Technologies, Sainte-Foy, Canada), so thermal influence can be neglected.

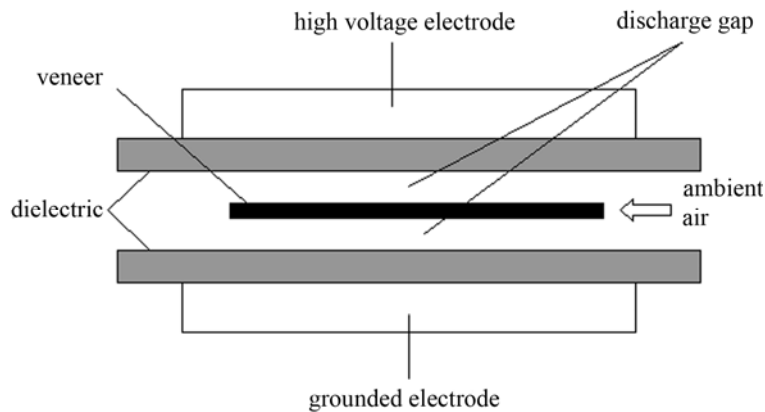


Figure 1: Plasma setup.

RESULTS AND DISCUSSION

Immersion tests in water were used to provide evidence for an accelerated water absorption of the veneers induced by the plasma treatment with durations of 0 s, 1 s, 2 s, 5 s and 10 s. The percentage increase in weight of wood veneers either untreated or treated with plasma for different lengths of time and submerged in water at 20°C for different lengths of time are given in Figures 2–5. Figure 2 shows the results for oak veneers. After treatment with plasma for only 1 s, the veneers showed slightly improved water uptake. But the difference between untreated and plasma-treated samples grew steadily and become more distinct with increasing time of the plasma treatment. The oak veneers treated with plasma for 10 s showed an improved water absorption of roughly 40%. Furthermore, the water uptake of samples that were immersed for 1 s and plasma-treated for 10 s was comparable with that of untreated veneers immersed for 60 s.

The beech veneers showed similar results, but with more pronounced differences between the untreated and plasma-treated samples (Figure 3). Treatment with plasma for 2 s achieved significant differences in water uptake and treatment for 5 s roughly doubled the water uptake for the first 10 s of immersion.

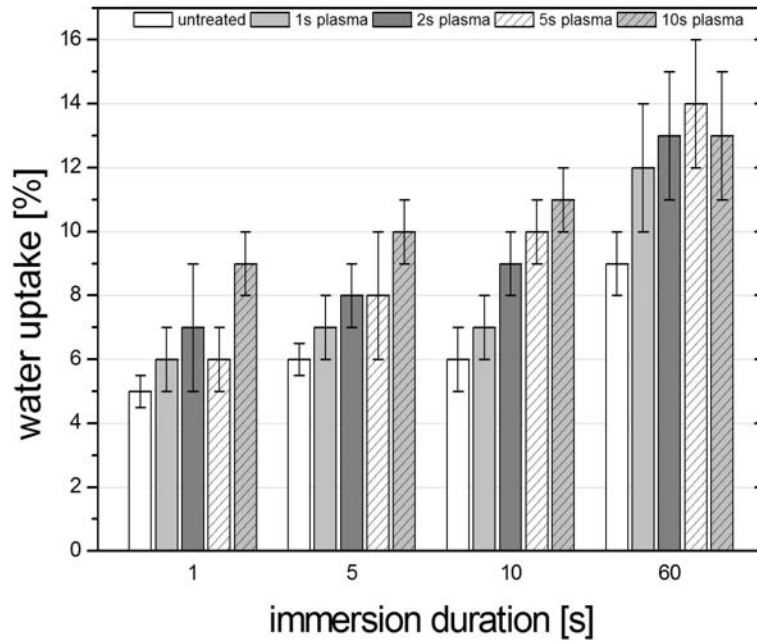


Figure 2: Water uptake of untreated and plasma-treated oak veneers after immersion in water for different lengths of time.

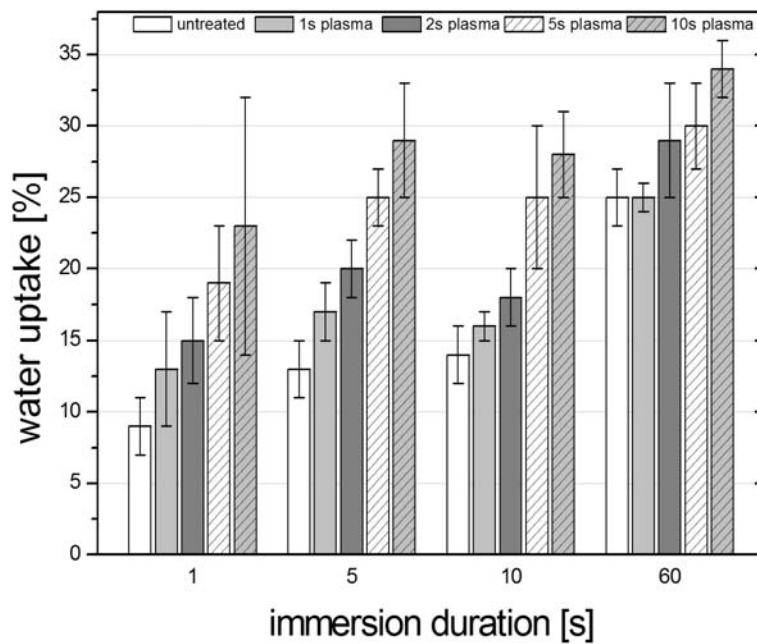


Figure 3: Water uptake of untreated and plasma-treated beech veneers after immersion in water for different lengths of time.

Very different results were obtained for the softwood (spruce and pine) veneers (Figure 4 and Figure 5). The water uptake increased with increasing immersion time, but no significant difference in water uptake was found between the untreated and the plasma-treated veneers.

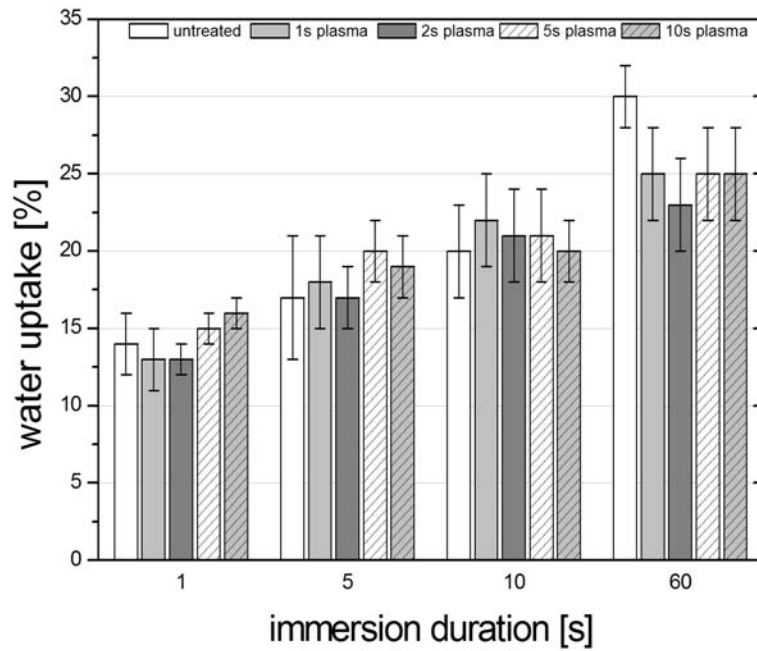


Figure 4: Water uptake of untreated and plasma-treated spruce veneers after immersion in water for different lengths of time.

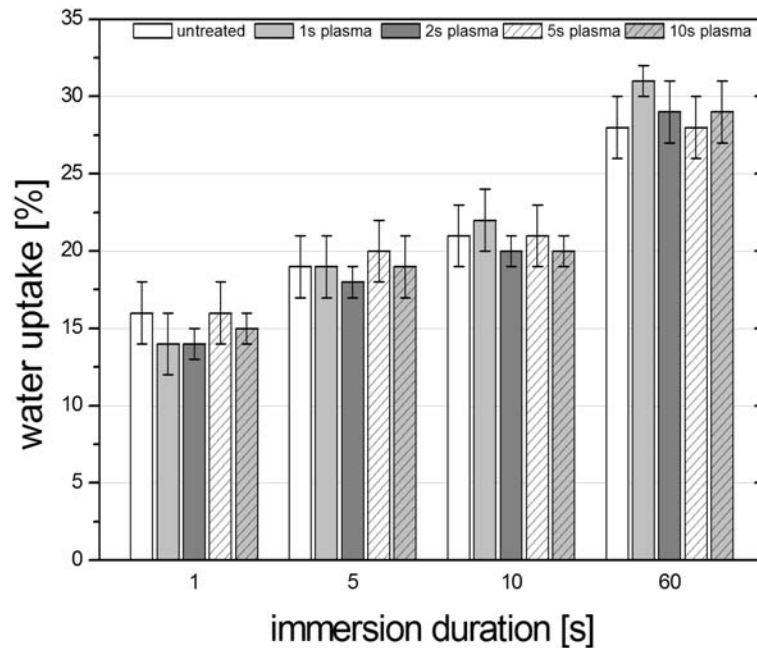


Figure 5: Water uptake of untreated and plasma-treated pine veneers after immersion in water for different lengths of time.

In preliminary tests, contact angle measurements and surface energy determination of plasma-treated wood surfaces revealed that different wood species react differently to treatment with plasma. To investigate whether treatment with plasma had the same effect on softwood and hardwood surfaces, contact angle measurements were done using water as the test liquid. Table 1 gives the results of the water contact angle

measurements on untreated veneers and veneers treated with plasma for 1 s or 10 s. Hardwood species showed a clear surface effect after treatment with plasma for 1 s, indicating increased surface energy. Even though the contact angles are decreased significantly, spruce and pine surfaces displayed a much weaker effect of treatment with plasma.

Table 1: Water contact angles

Sample	WCA (°)		
	Untreated	Plasma treatment 1 s	Plasma treatment 10 s
Oak	92 ± 6	43 ± 5	< 10
Beech	67 ± 8	< 10	< 10
Spruce	102 ± 6	77 ± 4	41 ± 4
Pine	99 ± 3	85 ± 14	62 ± 9

It is obvious that samples showing a strong surface effect also show a distinct change of water uptake. Therefore, the more inert softwood species were plasma-treated until a strong surface effect (WCA < 10°) occurred. After 60 s of treatment with plasma the WCA on spruce and pine was reduced to a level comparable to that of hardwood species after treatment with plasma for 10 s. On the basis of these results, the 60 s plasma-treated softwood species were expected to show a soaking ability similar to that of the hardwood species.

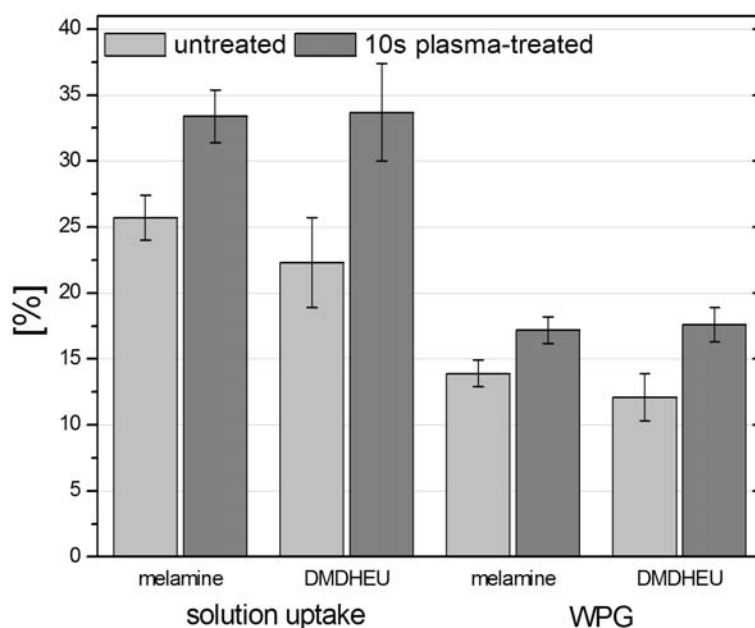


Figure 6: Immersion tests with untreated and plasma-treated beech veneers using melamine and DMDHEU as impregnation agents.

However, immersion tests with 60 s plasma-treated spruce veneers and pine veneers found no significant increase in water uptake compared to the untreated veneers (22±1% for the untreated and 25±2% for the 60 s plasma-treated spruce, 23±1% for the untreated and 22±2% for the 60 s plasma-treated pine). To determine whether these results can be transferred to immersion tests using waterborne impregnation agents, untreated and 10 s

plasma-treated beech and oak veneers were immersed for 10 s in 50% DMDHEU or for 10 s in 50% melamine solution. Any residual solution on the surface was removed by patting the samples with a cellulose tissue and then the samples were weighed. Both the melamine test and the DMDHEU test (Figure 6) showed a distinct gain in solution uptake and WPG for beech veneers; in particular, the DMDHEU test demonstrated enhanced soaking (+50% solution uptake and + 60% WPG). The same tests showed no significant increase in solution uptake or WPG for oak veneers: melamine uptake $15\pm 2\%$, WPG $8\pm 1\%$ for the untreated veneers and $15\pm 3\%$, WPG $8\pm 1\%$ for the plasma-treated samples; DMDHEU uptake $11\pm 3\%$, WPG $6\pm 1\%$ for the untreated veneers and $14\pm 2\%$, WPG $7\pm 1\%$ for the plasma-treated samples.

Further investigation of the plasma physics and chemistry and the anatomical and chemical properties of the wood species and their mutual reaction are needed to determine why different wood species react so differently to treatment with plasma.

CONCLUSIONS

The plasma-treated hardwood veneers showed a faster increase in weight due to faster water absorption compared to the untreated samples; however, great differences in the total amount of soaking and the impact of the plasma treatment exist between species. Treatment with plasma for 10 s had no effect on the soaking ability of the softwood species, although the water contact angle was distinctly reduced. Even treatment with plasma for 60 s to approximate the WCA of the plasma-treated hardwood surfaces showed no significant gain in water uptake. Beech veneers immersed in DMDHEU solution and in melamine solution were found to benefit from the treatment with plasma.

ACKNOWLEDGEMENTS

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The Durability and Weathering Performance of Wood Treated with Glutaraldehyde

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Keywords: Glutaraldehyde, crosslinking, dimensional stability; blue stain, fungal decay, natural weathering

ABSTRACT

In this study, Scots pine sapwood and European beech wood were treated with glutaraldehyde (GA) in aqueous solution using magnesium chloride as a catalyst in order to evaluate the durability towards staining and decay fungi and weathering. GA treatments to high weight percent gain (WPG) significantly restrained the growth of the blue stain fungus *Aureobasidium pullulans* on beech and pine wood in a test according to EN 152. Above 7% WPG, GA-treated beech wood did not display any mass loss due to incubation with the white rot fungus *Trametes versicolor*. The decay threshold of beech and pine samples towards the brown rot fungus *Coniophora puteana* was only 3% WPG. The average mass loss of the respective control samples was ca. 60%. During artificial weathering in a QUV over 168 h, GA-treated pine veneers strips underwent a lower tensile strength loss measured in a zero-span mode as compared to control veneers. The tensile strength of the treated specimens before weathering, however, was significantly lower than that of the controls because of strength losses due to GA treatment. FT-IR spectra revealed that GA treatment increased the photo-stability of lignin. This stability increased with increasing GA concentration. After 18 months of outdoor exposure, GA-treated pine wood panels displayed significantly less cracks than the untreated ones and took up less water in periodic submersion tests.

INTRODUCTION

Wood is susceptible to biotic attack and abiotic erosion when it is exposed outdoors. As an effective protecting strategy, chemical modification can partly alter the polymeric structure of the wood cell wall thereby improve the durability. Glutaraldehyde (GA; pentane-1,5-dial) is a dialdehyde which can in principle react with four hydroxyl groups in the presence of an acidic catalyst. Accordingly, GA has been used as a wood modifying agent using sulphur dioxide gas as a catalyst (Yasuda *et al.* 1994). Sulphur dioxide gas, however, is more difficult to control for wood treatment as compared to an aqueous system. Recently, an aqueous treating system containing GA and magnesium chloride as a catalyst has been successfully applied to promote the crosslink reaction (Xiao *et al.* 2010a). The GA-treated wood exhibited improved dimensional stability and reduced moisture sorption as compared to the untreated wood (Weaver *et al.* 1960, Fujimura *et al.* 1961, Yasuda *et al.* 1994, Xiao *et al.* 2010a). The anti-swelling efficiency (ASE) of GA-treated wood reached above 60% at a WPG of 13%; the equilibrium moisture content (EMC) and the capillary water uptake also considerably decrease (Yasuda *et al.*, 1994, Xiao *et al.* 2010a, Xie *et al.* 2010). GA-treated wood

(catalysis with sulphur dioxide) was shown to resist the decay by the brown-rot fungus *Tyromyces palustris* and the white-rot fungus *Trametes versicolor*. Two-ply laminated veneers treated with GA exhibited fewer surface cracks than the untreated controls after 24 week exposure to natural weathering or 720 h artificial weathering (Yusuf 1996). The objectives of this study is to further investigate the ability of wood treated with GA and magnesium chloride solution to resist against attack by staining and decay fungi and to assess the performance under artificial and natural weathering.

MATERIALS AND METHODS

Chemicals

Glutaraldehyde (GA) was supplied as a 50% aqueous solution in technical quality by BASF (Ludwigshafen, Germany). Magnesium chloride hexahydrate ($\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$) was extra purity grade. All other chemicals were of analytical purity grade.

Wood samples

(1) Blue stain testing: Scots pine (*Pinus sylvestris* L.) sapwood and European beech (*Fagus sylvatica* L.) wood measuring 40 mm × 40 mm × 5 mm (L × R × T); (2) basidiomycete testing: pine sapwood and beech wood with a size of 30 mm × 30 mm × 5 mm (L × R × T); (3) artificial weathering: pine sapwood micro-veneer strips measuring 100 mm × 15 mm × 80 μm (L × R × T). The preparation of micro-veneer strips was described previously (Xie *et al.* 2008); (4) outdoor weathering: pine vertical sawn panels with a size of 375 mm × 90 mm × 20 mm (L × R × T).

Treatment of wood

The samples were vacuum-pressure impregnated with aqueous acetate buffer solutions (pH 4.5, 0.1 M) respectively containing:

- (1) 0.4, 1.2, and 2.0 M GA and 6.0wt% $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ (related to GA) to treat the samples used for blue stain testing and natural weathering;
- (2) 0.4, 0.8, 1.2, 1.6, 2.0, and 2.8 M GA and 6.0wt% $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ (related to GA) to treat the samples used for brown- and white-rot testing.
- (3) 0.4, 1.2, and 2.0 M GA and 2.5wt% $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ (final concentration) as well as solely 2.5wt% $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ (final concentration) to treat the samples used for artificial weathering.

After impregnation, the excess solution was blotted off the samples with tissue paper and the samples were permitted to air dry to room moisture content. Subsequently, the samples were pre-cured at 80°C and finally cured at 120°C for a specific period, depending on the sample size. Samples treated only with acetate buffer served as controls. After conditioning (20°C, 65% RH) for 24 h, the samples used for blue stain, and decay testing were leached in the water according to the standard EN 84 and artificial weathering samples were rinsed with running tap water (approximately 40°C) for 2h to remove unreacted GA. The mass of samples was recorded and the resulting WPG calculated as described previously (Hill *et al.* 2004).

Blue stain testing

Blue stain testing was performed according to EN 152 (1988) but without prior weathering using a combined suspension of spores from *Aureobasidium pullulans* and *Sclerophoma pithyophila*. Ten replicates were used per treatment. After 8 weeks of incubation, the samples were evaluated and ranked (with rank 0: no growth to rank 5: heavy blue stain growth).

Basidiomycete decay testing

Basidiomycete decay testing was done according to a modified EN 113 (1996) test procedure. The test specimens were sterilized in an autoclave with water vapour at 104°C for 4 h and incubated for 16 weeks with *Coniophora puteana* (Schum.: Fr.) Karst. strain BAM Ebw. 15 (DSM 3085) and *Trametes versicolor* (Linneus) L. Quélet strain CTB 863 A (DSM 3086) respectively in Kolle flasks each accommodating a control specimen and a GA-treated specimen. Six replicates (flasks) were used per treatment.

Weathering of wood

For artificial weathering all micro-veneers were exposed in a QUV machine (Q-Panel, Lab Products, Cleveland, USA). The exposure involved to UV-A light (maximum absorption at 340 nm; 0.77 Wm⁻²nm⁻¹) from a fluorescent light source over 56 cycles, each including 2.5 h of UV irradiation at 60°C, and 30 min cold water spray (6-7 l min⁻¹). After 0, 48, 72, 96, 144, and 168 h 8 strips from each treatment were removed from the QUV and dry mass and zero-span tensile strength determined with a Pulmac paper tester (Pulmac International Inc., Middlesex, USA). FT-IR spectra of the veneers were recorded before and after weathering using attenuated total reflection (ATR) technique (DuraSanpIIIRITM, SensIR Technologies, Warrington, UK). Outdoor weathering was performed according to EN 927-3 (2006). Four panels were used per treatment which were end-grain sealed with a commercial sealant (Pyroprotect Schutzlack 2K, Rütgers Organics GmbH, Germany) and then exposed outdoors in Goettingen (Central Germany) from August 2008 to March 2010. Every 3 months all samples were weighed to determine the moisture content. After 18 months of weathering, the samples were withdrawn and conditioned at 20°C and 65% RH for 3 weeks. The panels were store on a sponge saturated with distilled water in a basin (20°C) and the weathered wood surface was about 2 mm under the water surface. Water uptake was determined gravimetrically after 1, 2, 6, 12, 24 h. The results were express as water uptake per square meter based on the weathered surface of the panels within the elapsed time. Surface cracking was evaluated according to standard ISO 4628 -4 (1982). The evaluation scale ranged from 0 to 5 (CR=0: no cracks and CR=5: dense pattern of cracks).

RESULTS AND DISCUSSION***Effect of GA treatment on blue stain infection***

Both the surface in contact to the vermiculite and the top surface of untreated pine samples were covered with blue stain fungi (rate 5). An increasing WPG reduced, but not eliminated, the growth of blue stain fungi on the bottom surface; the top surface exhibited less blue stain than the bottom surface (Table 1).

Table 1: Evaluation of blue stain on pine sapwood blocks (n=10; mean value (SD))

Conc.	WPG (%)	Bottom surface (vermiculite contact)	Top surface
Control	-1.3 (0.1)	5.0 (0.0)	4.9 (0.4)
0.4 M GA	2.0 (0.4)	3.8 (1.4)	2.8 (1.2)
1.2 M GA	10.9 (0.4)	1.3 (0.6)	0.0 (0.0)
2.0 M GA	19.2 (1.0)	1.6 (1.1)	0.3 (0.7)

Note: the value in the bracket showing standard deviation. Same in Table 2.

Table 2: Evaluation of blue stain on beech wood blocks (n=10; mean value (SD))

Conc.	WPG (%)	Bottom surface (vermiculite contact)	Top surface
Control	-1.7 (0.1)	4.6 (0.5)	3.1 (1.7)
0.4 M GA	-0.2 (0.2)	4.9 (0.4)	2.3 (0.5)
1.2 M GA	3.3 (0.2)	4.2 (0.9)	0.3(0.5)
2.0 M GA	7.0 (0.4)	3.4 (1.7)	0.1 (0.4)

The beech wood specimens treated with comparable GA concentrations as those from pine exhibited less resistance against blue stain infection, which might be attributed to the lower WPG obtained in beech wood compared to Scots pine (Table 2).

Effect of GA treatment on brown and white rot decay

The beech controls lost approximately 60% of mass during 16 weeks of incubation with the white rot fungus *T. versicolor*; GA treatment resulted in a gradual reduction in mass loss with increasing WPG. Above a WPG of about 7%, the mass loss of the beech specimens was less than 3% (Figure 1a). The brown rot fungus *C. puteana* induced a mass loss of about 50% for untreated beech and pine specimens (Figure 1b, c).

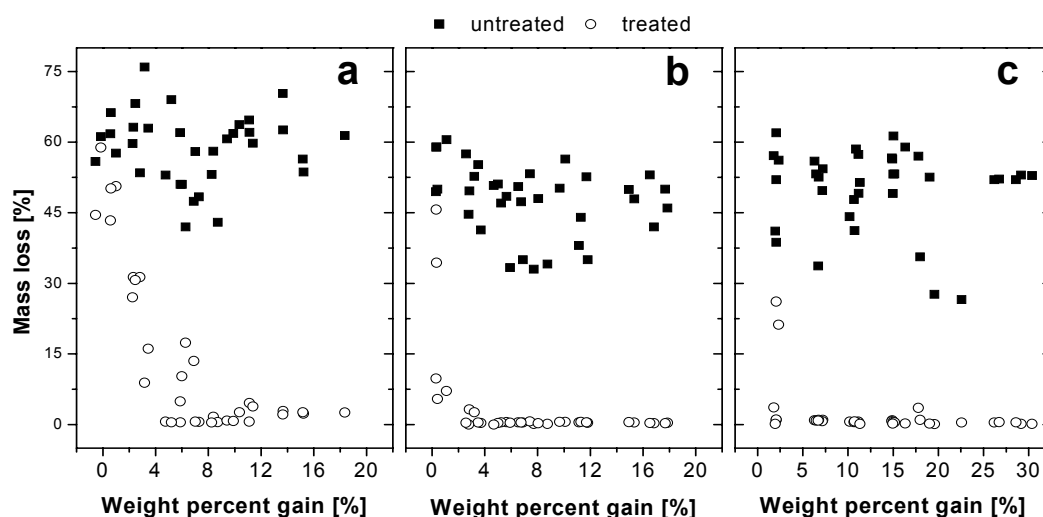


Figure 1: Mass loss of untreated or GA-samples after 16 weeks incubation with *T. versicolor* for beech wood (a), and *C. puteana* for beech wood (b) and pine sapwood (c).

The decay threshold *C. puteana* for both GA-treated wood species was very low. The specimens hardly ever exhibited any decay when the WPG was above 3%, suggesting that GA was more effective in preventing brown rot than white rot decay. The main reasons for the improved resistance of GA-treated wood against decay fungi have previously been attributed to reduction in the moisture content, substitution of hydroxyl groups of cell wall polymers, and blockage of nanopores in the cell walls due to cross-linking and bulking of the cell wall matrix (Hill 2009). Substitution of hydroxyl groups makes the cell wall polymers unrecognizable for enzymatic attack. The reduced pore size can make the swollen cell wall matrix inaccessible for enzymes or low molecular decay agents (Flournoy *et al.* 1991). Such improvements in fungal resistance normally occur at high WPG of ca. 20%, when the modification is based on simple hydroxyl blocking and bulking (Hill 2009). GA-treated wood, however, imparted decay resistance to pine wood already at 3% WPG which resulted in only 2% cell wall bulking. The effect of GA-treatment on fungal resistance is therefore mainly attributed to cross-

linking of the cell wall polymers as also shown for formaldehyde-treated wood (Stamm and Baechler 1960).

Artificial weathering of wood veneer strips

The infrared spectra of untreated wood show that the absorbance of the carbonyl stretching (1731 cm^{-1}), the aromatic skeletal stretching (1508 cm^{-1}), and the C-O stretching vibration (1265 cm^{-1}) in lignin diminished with the weathering time (Figure 2a); the aromatic vibration disappeared after 72 h weathering. Compared to the untreated controls, the stability of the carbonyl and lignin peaks in GA-treated wood was enhanced with increasing WPG (Figure 2b-c). Even after 168 h weathering, both the aromatic vibration (1508 cm^{-1}) and C-O stretching vibration (1265 cm^{-1}) were still visible in wood treated with 1.2 and 2.0 M GA (Figure 2c, d), which suggests that lignin was photo-stabilised due to GA treatment.

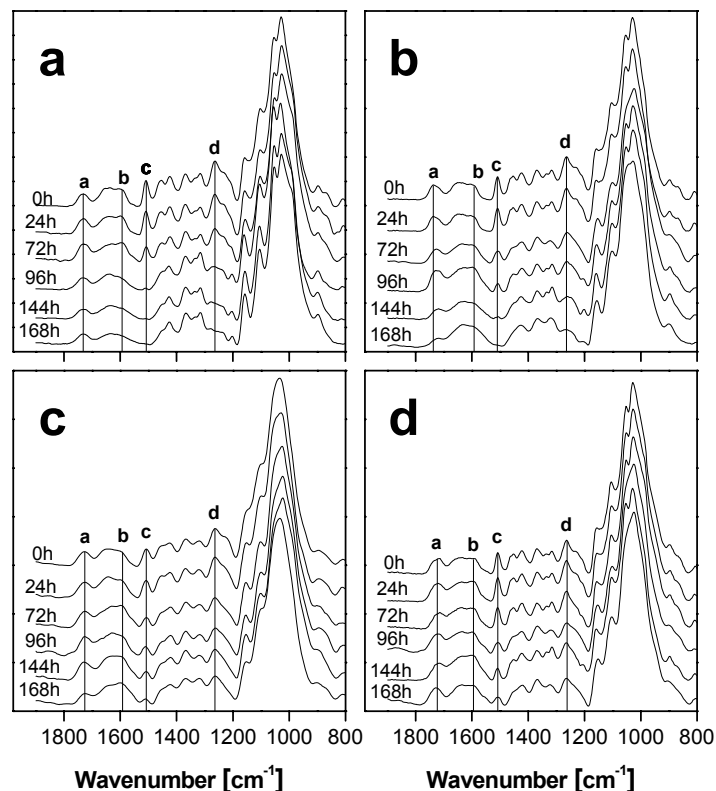


Figure 2: FTIR spectra of weathered veneers after different exposure times; veneers treated by acetate buffer (a), treated with 0.4(b), 1.2(c), and 2.0 M GA (d). FT-IR assignments: (a) carbonyl stretching; (b, c) aromatic skeletal vibration in lignin; (d) C-O stretching in lignin, acetyl and carbonyl vibration in hemicelluloses.

GA treatment reduced the tensile strength of micro-veneers; the strength loss increased with increasing GA content (0 h in Figure 3a). Treatment with the catalyst (MgCl_2) alone also reduced the tensile strength but in a minor degree. Wood treated with 2.0 M GA displayed 50% strength loss, which has been attributed to hydrolysis of cell wall polymers and cross-linking (Xiao *et al.* 2010b). With increasing weathering time, the untreated and solely catalyst-treated veneers continuously lost their strength. Strength loss of the GA-treated veneers, was much lower, especially in those veneers treated with high GA concentration (Figure 3a). The contribution of the treatment to the strength loss increased with increasing GA concentration but that of weathering decreased (Figure 3b). This might be due to hydrolysis of hemicelluloses and amorphous cellulose during

the modification which occurs in the untreated veneers primarily as a result of weathering.

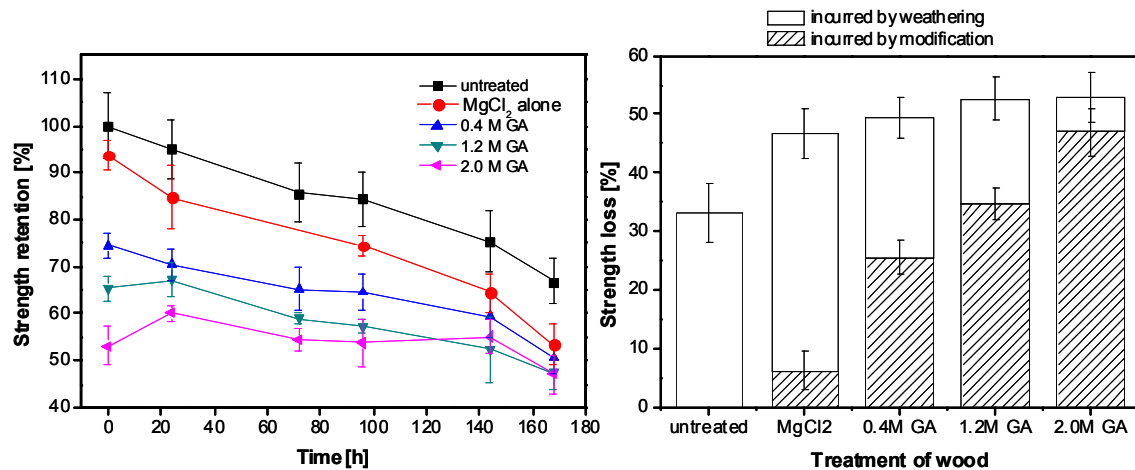


Figure 3: Tensile strength of veneers treated with buffer; 2.5% $MgCl_2 \cdot 6H_2O$ with acetate buffer, GA (0.4, 1.2, and 2.0 M) with 2.5 wt% magnesium chloride during artificial weathering in a QUV. All of treated solution pH value is 4.5 (n=8; error bars show SD).

Natural weathering of wood panels

The visual cracks on the untreated surface increased with the weathering period and were ranged CR=5 after 18 months of weathering (Table 3). Compared to the untreated panels, treatment with low GA concentration (0.4 M) considerably reduced surface cracking, but still some cracks were visible. There were no cracks visible on the wood panels treated with 1.2 and 2.0 M GA after 18 months weathering. The reduction in surface cracking can mainly be explained with the improved dimensional stability and reduced moisture sorption and water uptake (Xiao *et al.* 2010a). During the weathering period, the moisture content of the GA-treated panels was lower than that of the controls; it decreased and exhibited less fluctuation in the panels with higher WPG (Figure 4a). The periodical water submersion test showed that the panels took up smaller amounts of water with increasing GA content (Figure 4b). This may be due to the hydrophobing effect of GA (Xiao *et al.* 2010a) and due to fewer cracks on the surface of the treated panels.

Table 3: Surface crack ranking (CR) of wood after weathering. The cracking is classified into five levels according to ISO 4628-4, CR=0: no cracks; CR=1: very few cracks; CR=2: a few cracks permitted; CR=3: a moderate amount of cracks permitted; CR=4: a considerable amount of cracks permitted; CR=5: dense pattern of cracks (n=4).

treatment	Surface crack ranking (CR)					
	3 month	6 month	9 month	12 month	15 month	18 month
untreated	0	2	3	4	4	5
0.4 M GA	0	1	1	1	2	3
1.2 M GA	0	0	0	0	0	0
2.0 M GA	0	0	0	0	0	0

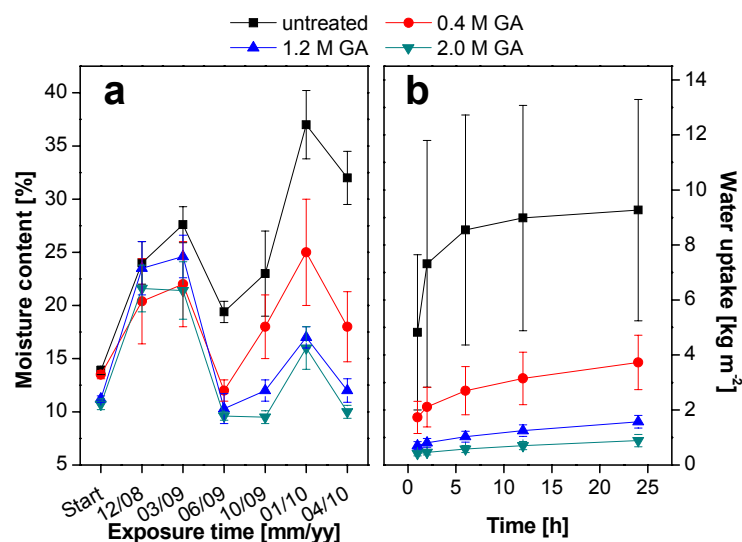


Figure 4: Moisture content of panels during outdoor exposure (a) and water uptake determined in a submersion test after 18 months exposure (b; $n=4$; error bars show SD).

CONCLUSIONS

GA-treatment reduces the colonisation of solid wood by blue stain fungi. The decay threshold of GA-treated wood for the degradation by white- and brown-rot fungi was much lower than that observed for modifications based on hydroxyl blocking and on bulking such as acetylation. Cross-linking of cell wall polymers is assumed to be the primary reason for the increased durability. GA-treatment enhances the photo-stability of lignin during weathering. The effect of weathering on photo-stabilisation of polysaccharides was not assessable by means of micro-tensile testing because the chemical treatment itself induced high strength loss. Treated wood exhibited fewer surface cracking and less moisture sorption and water uptake. GA is, thus, considered as a suitable modifying agent to improve the performance of wood used outdoors.

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Liquids and Coatings Wettability and Penetrability of Acetylated Scots Pine Sapwood

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ABSTRACT

In most outdoor applications, acetylated wood requires a surface treatment by means of *e.g.* film-forming coatings or semi film-forming stains and oil treatments. The main reasons are to preserve the aesthetic value of the acetylated wood and to ensure a rational maintenance, that is to protect against mould growth, dirt and other types of uneven discoloration effects. In this case, the adhesion capacity of the coatings or stains in the acetylated wood substrate is of great importance. The adhesion mechanism for wood-coating systems is complex, and includes several key factors such as liquid wettability and penetrability of the wood. The aim of this study is to add some insight about important factors governing coatings adhesion to acetylated Scots pine sapwood. The Wilhelmy plate principle was applied as a means for estimations of the wood surface wettability as well as sorption and capillary actions for water and two different stains, one water-based and one solvent-based. Penetrability information of the stains was gained by microscopic analysis of the actual wood-coating interphase morphology.

INTRODUCTION

A poor adhesion or anchoring capacity of coatings in acetylated wood may result in wood-coating delamination effects, especially after cyclic weather conditions and resulting movements in the surface layer of wood. Many different adhesion theories have been proposed and applied in the adhesion science and technology field (Shultz and Nardin 1999). This work involves the wetting (or adsorption) theory which we believe have the potential to add new and valuable information about liquids and coatings wettability and penetrability of modified wood. The wettability of materials can be characterized by parameters such as contact angles, surface free energy and work of adhesion. For substrates like wood it is important to remember that wetting phenomena also involves capillary actions, *e.g.* penetration of liquids or *e.g.* coatings into the porous structure of wood or along its irregular and rough surface structure (Liptáková and Kúdela 1994). Some further aspects of wetting phenomena on unmodified wood has been reported and reviewed by *e.g.* Wålinder and Gardner (2002) and Bryne and Wålinder (2010). The main conclusion and recapitulation of these studies is that there exist a number of typical “pitfalls” that easily interfere measurements of wetting parameters on wood, mainly due to its complex heterogeneous, porous, rough, hygroscopic and anisotropic nature. Because of this complexity of a wood surface it is therefore more accurate to refer to *apparent* wetting parameters, which must be rigorously determined with a control of the strongly influencing factors such as probe liquid contamination (due to the wood extractives), wicking and bulk sorption effects.

The wettability and theoretical adhesion capacity of acetylated Scots pine in relation to certain adhesives and thermoplastic polymers have recently been studied by Bryne and Wålinder (2010). Little information is, however, available linking the wettability properties with coatings and stains penetrability of such acetylated wood. The main objective of this paper is therefore to add some insight about important factors governing coatings wettability and penetrability which is believed to be strongly linked to their adhesion and anchoring ability to acetylated Scots pine sapwood. Another purpose of this presentation is to present and demonstrate some of our experience and some principles regarding the wetting theory in combination with micro morphological observations as a means for studying coatings adhesion capacity on modified wood.

EXPERIMENTAL

Acetylated wood samples and preparation of specimens for the wetting experiments

The modified wood material chosen for this study was acetylated Scots pine (*Pinus silvestris* L.) sapwood boards of the original dimensions 1200 x 150 x 25 mm³, produced by A-Cell AB in year 2004 in an acetylation pilot plant at Chalmers (from 2008 placed at SP in Borås). The reaction vessel in this plant is microwave heated and of the volume 0.67 m³. The method of acetylation followed a simplified procedure without use of any catalyst or co-solvent in the reaction (Larsson Brelid 1998). The acetylation level was approximately 18–23% expressed as wood acetyl content. Control sample boards were also selected from the same batch as for the acetylated boards.

From selected boards with approximately the same annual ring structure, smaller samples with dimensions of ca 6–9 mm in the radial (R) direction, ca 120 mm in the tangential (T) direction (following a band of approximately 6–7 annual rings), and ca 30 mm in the longitudinal (L) direction were prepared with a band saw and hand veneer saw. To eliminate liquid sorption through the specimen's end-grain during the wetting experiments one cross section of these samples were sealed with a polyurethane coating. From these samples the final specimens for the wetting experiments were prepared using an ordinary wood chisel to cut radial sectioned veneer replicates with dimensions of approximately 30 × 9 × 1 mm³ (acetylated sample) and 30 × 6 × 1 mm³ (control sample) in the L, R and T directions, respectively. Based on the dry weight of the wood, the moisture content of the acetylated and control specimens was approximately 2–3% and 6–7% respectively. Supplementary details about the preparation of suitable wood samples for the wetting experiments can be found in Wålinder and Gardner (2002).

Wetting experiments by the Wilhelmy Method

The Wilhelmy method, using a Sigma 70 tensiometer from KSV Instruments, was applied to estimate the wetting and sorption properties of the veneers regarding water and two different stains. The veneers were immersed along the grain in the liquids (advancing stage) to a depth of 10 mm and then withdrawn (receding stage) to about 4 mm above the surface. For the measurements in water the specimens were immersed a second time to examine if complete wetting (zero contact angle) occurred for the receding stage. The immersion and withdrawal velocity was 12 mm/min. The measurements were performed at about 22°C and about 50% relative humidity. The main principle of the Wilhelmy method and a so-called Wilhelmy test cycle and plot (hereinafter denoted a Wilhelmy plot) are shown in Figure 1. Figure 1 also defines the constants, wetting parameters and force balance relations used in this study.

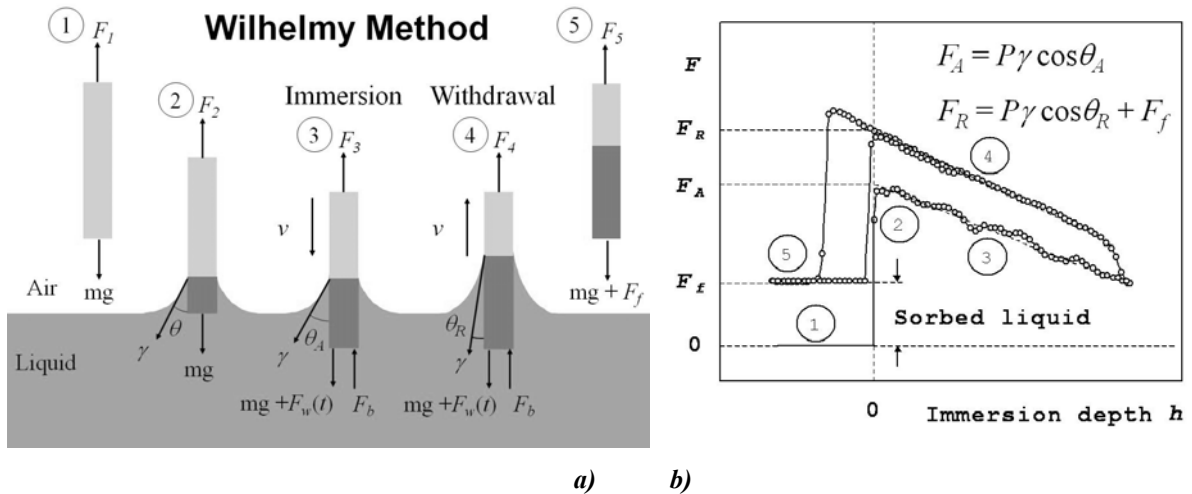


Figure 1: a) Schematic illustration of the Wilhelmy method and the corresponding force (F) balances for studying the wettability of a sorbing material such as a wood veneer. m = mass of the specimen, g = gravitational constant, P = perimeter of the specimen, γ = surface tension of the liquid, θ = apparent contact angle (A denotes advancing and R receding), $F_w(t)$ = sorbed liquid at time t , ρ = liquid density, A = cross-sectional area of the veneer, h = immersion depth, F_f = final weight change due to liquid sorption, and v = velocity of immersion and withdrawal. At low velocities it is assumed that a dynamic contact angle is approximately equal to the corresponding static contact angle. b) The Wilhelmy method illustrated by a schematic plot of the recorded weight change (or force change F) versus immersion depth h during a test cycle when a wood veneer is immersed in and withdrawn from a liquid. The abbreviations are explained in Figure 1. (From Wälinder and Gardner 2002)

First, Wilhelmy test cycles for 15 specimens, *i.e.* replicate veneers prepared as described above of both the acetylated and the control wood, were run in water with a surface tension of ca 72.0 mN/m. For each measurement new fresh water was used. All the measurements in water were performed within 5 minutes from the specimen preparation. Thereafter, to determine the perimeter of each specimen corresponding Wilhelmy test cycles were run in the ‘wetting-out liquid’ octane with a surface tension of ca 21.5 mN/m. Before these perimeter estimations, each specimen was conditioned to approximately the same moisture content and weight as before the first water wetting measurement. Subsequently, all specimens were once again conditioned to reach their initial weights. 5 specimen each of both the acetylated and the control wood sample were then tested in two different semi film-forming or semi-transparent stains for outdoor use: one water based (Beckers Fasadlasyr, alkyde-akrylate hybride, brun/brown 9075, article no. 041082) and one white spirit based (Bojens Uteasyr, alkyde oil, mellanbrun/light brown, article no. 07.08-2.26). All the measurements in the stains were performed approximately 24 hours after the specimen preparation and the measurements in water. After the Wilhelmy test cycle in the stains the coated specimens were mounted vertically in a jig to air dry and cure over-night at normal room temperature. The determination, or rather estimation, of apparent water contact angles on the veneers, the perimeter of the veneers, as well as the liquid or coating sorption, followed the procedures described in more detail by Wälinder and Gardner (2002). To study any possible contamination of the probe liquids by wood extractives that may occur during the liquids wetting and sorption measurements a so-called apparent surface tension γ_{app} was calculated from the receding part of the test cycle. A lower value of γ_{app} than the initial surface tension of probe liquid indicates that wood extractives interfere the measurements of the wetting forces, especially at the wood-liquid interface.

Micro morphological studies of the wood-coatings interface

To study the specimen surface micromorphology as well as the coatings penetration depth and pathways and micromorphology of the wood-coating interphase (or interfaces), transverse sections of both the coated and uncoated specimens were prepared by a contact free cutting technique, *i.e.* a surface micromachining procedure based on UV laser irradiation. See further experimental set up details and principles for this technique described by Wålinder *et al.* (2009). Scanning electron microscopy (SEM) was used to evaluate the microstructure of the prepared the samples. The apparatuses were a Hitachi Tabletop Microscope TM-1000. Both the UV-laser prepared cross sections of the uncoated and coated veneer specimens as well as their flat sides were examined.

RESULTS AND DISCUSSION

Figure 2 shows some example SEM micrographs of the cross section and radial section (flat side) of the prepared wood veneer specimen. No distinct difference could be observed by this SEM analysis between the modified and control specimen microstructure. It is obvious that the general flat side specimen surface, valid for both the acetylated and the unmodified samples, consist mainly of the middle lamella of the wood tracheids. As expected, when such radial sections are prepared by a wood chisel the fracture goes predominantly in the middle lamella between the radial oriented wood cell rows. It is important to bear this in mind since such surfaces will have a higher lignin fraction than *e.g.* ordinary cross sections of wood. Hence, the effect of the acetylation modification should be pronounced in such surfaces, due to the fact that lignin is the wood polymer component which undergoes the highest substitution of hydroxyl groups during the wood acetylation process (Rowell 1994).

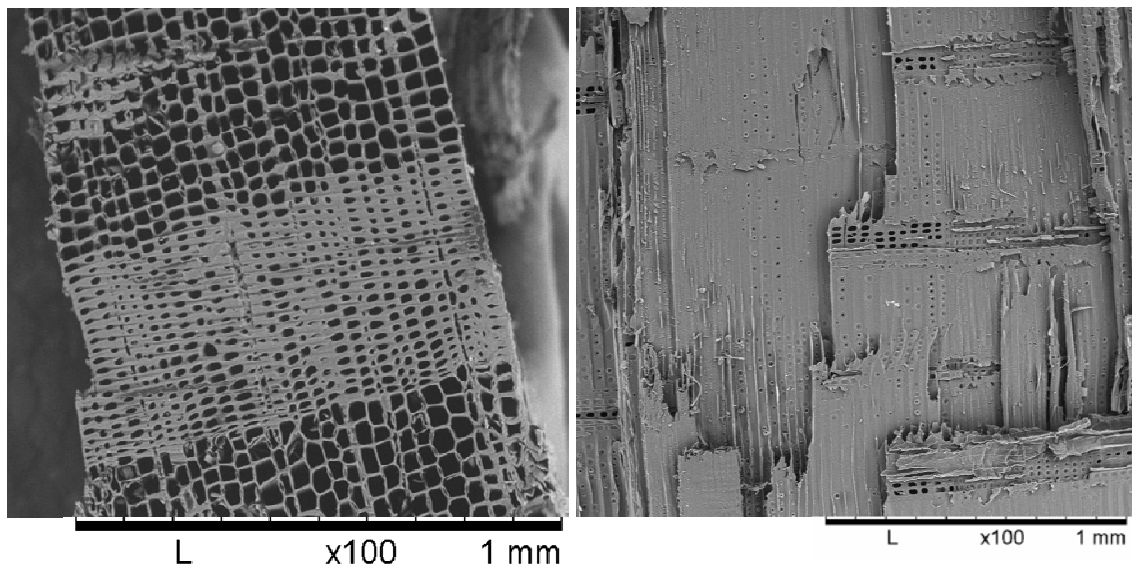


Figure 2: Example SEM-micrographs of the structure of the specimens studied in the wetting and sorption experiments: left) cross section (prepared by UV laser ablation); and right) radial section (cut by wood chisel). Note the different scale bars.

Figure 3 shows some example Wilhelmy plots for the wetting and sorption experiments in octane and water. Note that in contrast to the schematic plot shown in Figure 1, the force value on the Y-axis in these plots has been normalized by the circumvented length, or perimeter, of each specimen. A number of obvious features can be observed

from these plots. On one hand, the wetting and sorption measurements in the wetting-out liquid octane result in no clear differences between the acetylated and the control specimens, as can be seen in the two graphs to the left in Figure 3. This is mainly illustrated by the shape of the advancing curves and the absence of hysteresis effects when the advancing mode is changed to the receding mode, indicating that no finite contact angle exists. It can also be seen that the final sorbed liquid is in the same range for the two samples, which indicates that there is no great difference between their permeability for such a non-polar low surface tension liquid. On the other hand, the measurements in the high surface tension and highly polar liquid water result in clear differences between the acetylated and the control specimens, as can be seen in the two graphs to the right in Figure 3. This is mainly illustrated by the wetting force level, F/P , of the advancing curves and the clear difference in hysteresis effects when changing from the advancing to the receding mode. As can be seen, the acetylated sample exhibits a distinctly lower level of the advancing part of F/P versus depth plot and much greater hysteresis effect, which proves that the acetylated wood has a distinctly higher contact angle and lower water wettability than the unmodified control. Similar results for Scots pine have also been reported by Bryne and Wålinder (2010). Another observation which also is illustrated in Figure 3 is that the acetylated specimens have ca 50% lower level of sorbed water after a test cycle compared with the controls. Note that this water sorption involves both capillary and diffusion transport processes transverse the fiber direction and longitudinally mainly in the surface layer along the wood tracheid structure. In this case it seems as though the permeability for capillary transport of liquids in the transverse direction is pretty low and not significantly different between the acetylated and untreated samples, which are in coherence with the micro morphological observations of penetration the stains as presented below. It is therefore suggested that the distinctly lower water sorption in the acetylated samples in this case is directly linked to the lower hygroscopicity or affinity for water uptake by diffusion compared with the controls, and not to any differences in their permeability for transverse capillary transport of water. Table 1 summarizes mean values and standard deviations of some resulting wetting and sorption parameters regarding the discussion above and from the analysis of the Wilhelmy plots in octane and water as exemplified in Figure 3. One additional observation is that the apparent surface tension during the receding part of the Wilhelmy test cycles in water is distinctly lower for the control samples. This indicates a strong interference by wood extractives at the wood-water interface for the unmodified pine sapwood sample as compared with the comparably low corresponding extractives interference for the acetylated sample. Figure 4 shows some examples of Wilhelmy plots of the acetylated wood sample in the two different stain systems. In this case no notably differences could be observed between the acetylated and the control samples regarding these two stains wettability and sorption properties. However, as expected a great difference can be seen between the wetting and sorption behavior of the water-based system compared with the solvent-based system. Tables 2 and 3 summarize the results from the wetting and sorption experiments in the two different stains. Figure 5 shows some example SEM micrographs of the cross section of the coated wood specimens. The SEM analysis showed clearly that the penetrability was remarkably low in the transverse direction of both the acetylated and unmodified samples and for both the water and solvent-based stain systems studied. No significant difference in the penetrability pattern of the two stains could be seen between the acetylated and the control samples. As shown in Figure 5, a more pronounced and thicker film was formed in the specimens coated with the water-based stain system. A better anchoring of the stains could also be noticed in the outer wood cell layer in some portions of earlywood

in both the acetylated and the control wood samples. This was due to the fact that these earlywood portions had damage outer cell walls, originating from the sample preparation, which created a pathway for stain penetration.

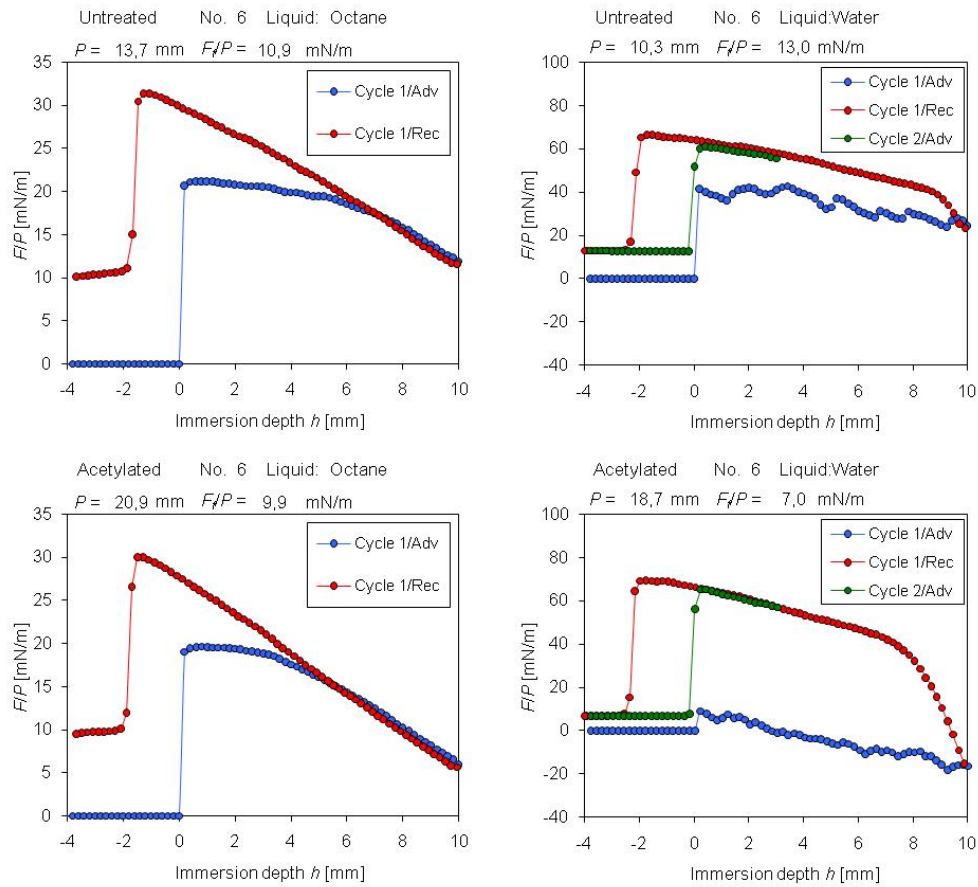


Figure 3: Examples of Wilhelmy test cycles in the wetting-out liquid octane (the two left diagrams) and the probe liquid water (the two right diagrams) for the unmodified controls (the two upper diagrams) and the acetylated (the two lower diagrams) Scots pine sapwood samples.

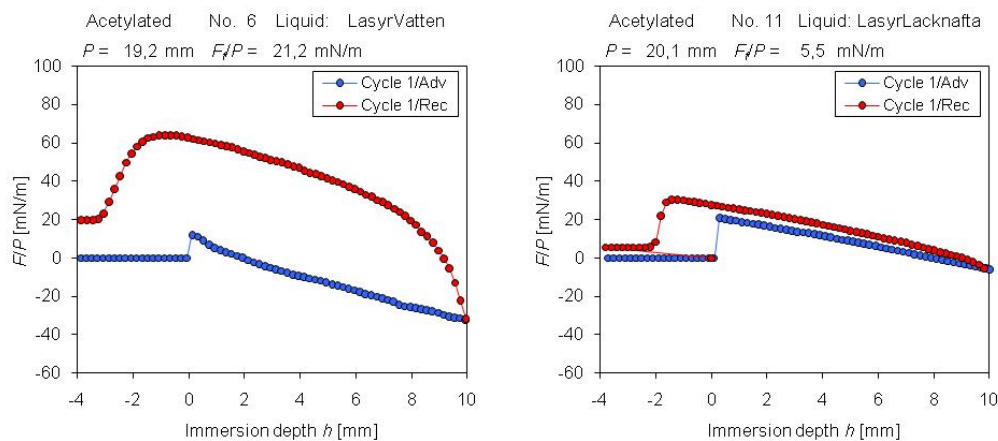


Figure 4: Examples of Wilhelmy test cycles in the water-based stain (the left diagram) and the white spirit-based stain (the right diagram) for the acetylated Scots pine sapwood samples.

Table 1: Estimated apparent wetting (θ , γ_{app}) and sorption (F_f/P) parameters for water and octane in contact with untreated and acetylated Scots pine sapwood. Std = standard deviation.

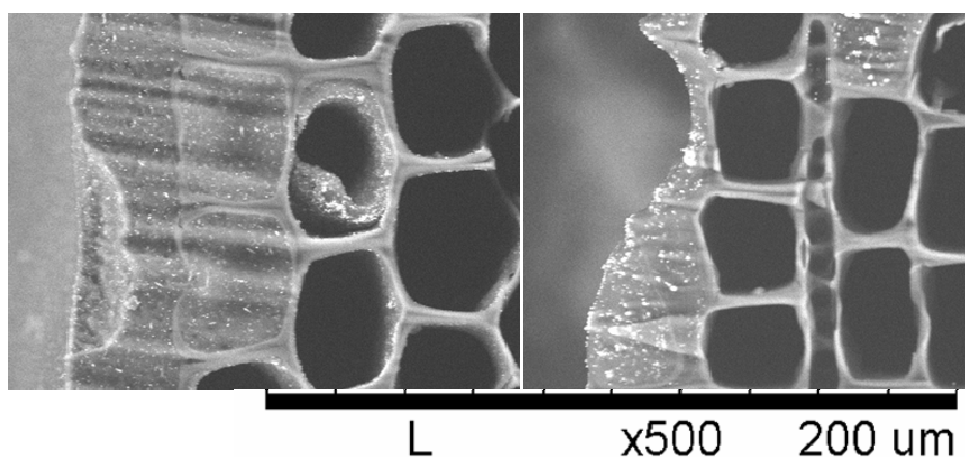
Treatment	P		γ_{app}	F_f/P		Water		
	Octane	Water		Octane	Water	F_A/P	$\cos \theta$	θ
Untreated	14,5	10,6	52,8	10,6	12,4	36,7	0,5	59,7
Std	0,6	0,7	2,8	0,6	2,1	4,5	0,1	4,1
Acetylated	20,5	18,2	64,5	10,5	7,7	10,7	0,1	81,5
Std	1,0	0,6	2,2	0,7	1,5	5,1	0,1	4,1

Table 2: Estimated apparent wetting (θ , γ_{app}) and sorption (F_f/P) parameters for a water-based stain in contact with untreated and acetylated Scots pine sapwood. Std = standard deviation.

Treatment	P		γ_{app}	F_f/P		Stain water-based		
	Octane	Stain water-based		Octane	Stain water-based	F_A/P	$\cos \theta$	θ
Untreated	14,2	13,1	50,9	10,6	20,9	7,3	0,1	81,6
Std	0,5	1,1	1,2	0,3	2,7	1,5	0,0	1,7
Acetylated	20,5	17,9	47,0	10,1	20,9	10,5	0,2	78,0
Std	1,1	1,0	2,2	0,4	0,7	1,6	0,0	1,9

Table 3: Estimated apparent wetting (θ , γ_{app}) and sorption (F_f/P) parameters for a white spirit-based stain in contact with untreated and acetylated Scots pine sapwood. Std = standard deviation.

Treatment	P		γ_{app}	F_f/P		Stain white spirit-based		
	Octane	Stain white spirit-based		Octane	Stain white spirit-based	F_A/P	$\cos \theta$	θ
Untreated	14,9	14,8	26,7	10,1	6,0	22,5	0,8	32,7
Std	0,7	0,7	0,7	0,6	0,5	0,8	0,0	3,1
Acetylated	20,2	20,5	27,3	9,3	5,4	21,5	0,8	36,5
Std	0,5	0,6	0,9	0,6	0,4	0,7	0,0	2,5

**Figure 5: Example SEM-micrographs of stain penetrability in the coated specimens (left side of the two micrographs): water-based stain (left); and white spirit-based stain (right)**

CONCLUSIONS

The results from these wetting, sorption and micro morphological studies demonstrates that the permeability for capillary transport, or penetrability, was remarkably low in the transverse direction of both the acetylated and unmodified Scots pine sapwood and for both the water and solvent-based stain systems studied. A better anchoring of the stains could be observed in the outer wood cell layer in some portions of earlywood in both the acetylated and the control wood samples. This was due to the fact that these earlywood portions had damage outer cell walls, originating from the sample preparation, which created a pathway for stain penetration. Future studies is suggested to relate these results to some practical adhesion test of the wood-coating interfaces, preferable by cyclic water saturation and drying exposure of UV-laser ablated cross sections of the coated veneer samples combined with micro morphological studies of the cross sections before and after such an exposure.

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Resistance of Modified Wood to Marine Borers

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ABSTRACT

The resistance of chemically modified wood was assessed in a field test according to European Standard EN 275 over a period of two years at sites in the North and the Baltic Sea. Scots pine (*Pinus sylvestris*) sapwood was treated with DMDHEU (1,3-dimethylol-4,5-dihydroxy-ethylen-urea), MMF (methylated-methylol-melamine) and TEOS (tetra-ethoxy-ortho-silane). In addition, acetylated and untreated Radiata pine (*Pinus radiata*) was included in the test. The content of the modification agent in the exposed samples was determined annually in order to determine the stability of treatment during the exposure in seawater. Constant chemical contents indicated that leaching of chemicals did not occur. The common shipworm (*Teredo navalis*) was the only wood boring organism found at the two test sites. While the controls were severely infested, modified specimens showed no to moderate attack by *T. navalis*. Additionally, the resistance of the modified wood to the gribble *Limnoria quadripunctata* was evaluated by means of a forced feeding laboratory test, in which faecal pellet production served as a measure of feeding rates. Resin treatments (DMDHEU, MMF) required a weight percent gain (WPG) above ca. 15 % to attain pellet production rates considerably lower than the untreated control specimens. The pellet production rates on acetylated Radiata pine (ca. 30 % WPG) were comparable to those on the more resistant resin treated samples, while they were only slightly lower on TEOS treated wood (ca. 25 % WPG) as compared to the controls.

INTRODUCTION

An adequate service life of wooden structures in the sea is ensured only, if wood is treated with biocidal wood preservatives or if tropical hardwoods are used that are naturally resistant against wood borers. Wood preservatives face increasingly severe legal restrictions and a poor public image. The use of well known durable tropical timbers is questionable, as it might contribute to deforestation. It has been shown in earlier studies that wood modification can enhance the resistance to marine borers. Johnson and Rowell (1988) found that wood treated with propylene oxide, butylenes oxide and acetic anhydride (ca. 20 % WPG) were very resistant in a field trial. Larson Brelid *et al.* (2000) also tested acetylated wood and found considerably lower resistance at a comparable acetyl content. Westin *et al.* (2007) conducted a field trial on a large number of different modification methods in which furfurylation, acetylation and MMF (methylated-melamine-formaldehyde) performed best. Modification with linear chain carboxylic acid anhydrides reduced feeding rates of *Limnoria quadripunctata* in a short term laboratory test (Papadopoulos *et al.* 2008). Borges *et al.* (2005) showed that a

similar test design gave – “in most cases” - good predictions of the performance of DMDHEU (dimethylol-dihydroxy-ethylen-urea)- and PBTC (phosphobutane tricarboxylic acid)- modified wood in a field trial.

In northern European seas, wood is primarily attacked by crustacea of the genus *Limnoria*, called gribbles, and bivalves of the genus *Teredo*. Due to different reproductive strategies (Nair and Saaraswathy 1971, Cragg 2003) shipworm larvae are abundant at most test sites. Gribble activity is less likely. In this study, the resistance of differently modified wood to shipworms and gribbles was evaluated in a field trial and a laboratory test, respectively.

EXPERIMENTAL

Wood treatment

Commercially available acetylated Radiata pine (*Pinus radiata* D. Don) (Accoya®; Titanwood Limited, Netherlands) and DMDHEU treated Scots pine (*Pinus sylvestris* L.) (Belmadur®; BASF) were supplied by the manufacturers. Additionally, Scots pine samples were impregnated with MMF, TEOS (tetra-ethoxy-silane) and acid copper chromate using a lab-scale impregnation vessel. TEOS was applied in sol state as described by Donath *et al.* (2004). The acid copper chromate (Cu Cr) was prepared from CuO and CrO₃ with the same concentrations of Cu and Cr as the alternative reference preservative according to the European Standard EN 275 (1992), which is made of CuSO₄*5H₂O, K₂Cr₂O₇ and CrO₃. The preservative treated specimens were stored at room temperature for 8 weeks to ensure fixation of the chemical.

Field trial

Test sites

Two marinas served as test sites, of which one is situated in the North Sea (Wilhelmshaven, Germany; 53° 31' N, 8° 09' E) and the other in the Baltic Sea (Hejlsminde, Denmark; 55° 21' N, 9° 36' E). Salinity ranges between 28 PSU (practical salinity unit) and 33 PSU at the first and between 15 PSU and 25 PSU at the second site. Water temperature in both locations varies between 0...5 C in January and 20...25°C in August with four to five months per year above the common shipworm's spawning temperature of 14°C (NERI 2010, Nair and Saaraswathy 1971).

Installation and evaluation of specimens

Small panels measuring 200 x 75 x 25 mm (l x r x t) were attached to ladder like racks made of construction steel. Plastic tubes of 25 mm length served as spacers between the specimens. The racks were attached to a landing stage at 2...4 m below medium high tide.

The test was started in May 2008. The samples were examined annually in winter or spring. At each inspection, the fouling on differently treated samples was compared. Then the fouling organisms were carefully removed with a scraper and the specimens were X-rayed and put back into the sea. Additionally, five untreated controls of Scots pine sapwood are exposed. Some rejected controls were used to identify the shipworm species. In Wilhelmshaven, the racks were stored in an outdoor pool during the winter to prevent the racks from being damaged by ice. X-rays were recorded in batches during

this period. Each specimen was rated according to the system shown in Table 1. The mean value of the ratings for all replicates gave the notional average rating for the respective treatment.

Table 1: Rating system for attack by Teredinids and other molluscs according to EN 275

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

Determination of chemical contents

The chemical content of the specimens used in the field test was determined on panels not exposed to sea water, exposed for one year and after two year exposure. For this purpose, a hole, 10 mm in diameter, was drilled into a corner of each panel and about 1 g of the wood powder was collected for analysis.

The acetyl content of the acetylated wood was calculated from the amount of acetic acid determined by HPLC (Breeze System, Waters Corporation, Milford, USA with Aminex HPX-87H column, Bio-Rad Laboratories Inc., Hercules, USA) after saponification with 0.5 M NaOH. For DMDHEU- and the MMF-treatment, the N/C-ratio served as a measure of the chemical content. The CHN analyzer Vario EL III (Elementar Analysensysteme GmbH, Hanau, Germany) was used to determine the nitrogen-and carbon-content of the samples. The chemical retention of silicate in wood formed from TEOS was assessed as acid insoluble ash referring to DIN 54373 (1989). The references' copper content was determined by ICP-OES (Inductively Coupled Plasma - Optical Emission Spectroscopy, Ciroc CCD, SPECTRO Analytical Instruments GmbH, Kleve) after decomposition by acid hydrolysis.

Laboratory assay

Feeding test

Wood sticks measuring 20 x 2.5 x 4 mm³ from each material tested in the field trial were cut from spare panels. They were vacuum-impregnated with sea water and leached for 14 days. A 12-well culture dish was prepared for each material. A stick was placed in each well, along with 5 ml of sea water and a single specimen of *Limnoria quadripunctata*. Pellets produced by the gribbles feeding on the sticks were counted twice a week at 3- and 4-day intervals. Each time the water in the wells was changed. Additionally, half of the water was changed in the middle of the 4 day period to avoid accumulation of substances leached from the sticks. As moulting suppresses feeding, data from the counting intervals in which moulting took place were excluded from analysis. Also, intervals during which animals died were not taken into account. A

material's resistance to *L. quadripunctata* was assessed on the basis of the average amount of faecal pellets produced per day.

Choice test

A choice test was set up to evaluate the influence of leached copper on the pellets production rate of animals feeding on preservative treated sticks. Sticks treated with 1.2 % acid copper chromate and untreated controls of Scots pine were cut into half. Five cell culture dishes were prepared with an identical setup: Each container included wells with treated samples (n = 4), untreated samples (n = 4) and both treated and untreated samples (n = 4). Pellets were counted after three and seven days. Additionally, the concentration of copper and chromium in the water after 3 days was determined by ICP-OES.

Statistics

Chemical retentions and faecal pellet production rates were not normally distributed. Thus the median was chosen as a measure of central tendency; 95 % confidence intervals were calculated as suggested by McGill *et al.* (1978):

$$M \pm 1.7 \frac{1.25R}{1.35\sqrt{N}} \quad (1)$$

where M is the median; R is the interquartile range; and N is the number of observations. If the confidence intervals of “two medians do not overlap the medians are, roughly, significantly different at about a 95% confidence level.” (McGill *et al.* 1978).

RESULTS AND DISCUSSION

Field test

Chemical retention

Figure 1 shows the chemical contents of specimens exposed in sea water for different periods of time. The different measures were indexed to the median of the non-exposed controls. It should be noted that for each exposure time a different group of samples was analysed. All samples of the same treatment, however, originate from the same batch. So far, all treatments seem to be stable even under the severe conditions in marine environments. Further measurements will show, if there is a downward tendency for the chemical contents of Accoya, Belmadur (0.8 M) and CuCr (1.2 %).

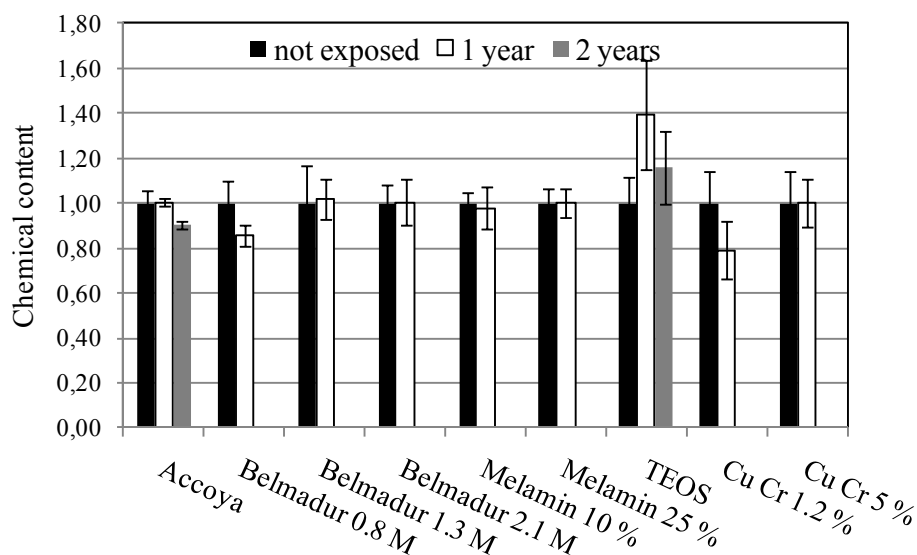


Figure 1: Chemical contents of non-exposed controls and specimens exposed for one and two years, respectively. (Median \pm 95 % confidence interval; n = 10)

Attack by wood borers

At both sites wood samples were attacked only by the common shipworm *Teredo navalis*. Crustacean borers or other wood boring bivalves were not found. Attack by shipworms, however, was severe. All untreated controls were destroyed after two years (Table 2). All panels treated with the reference preservative (CuCr) were sound in Hejlsminde, but those treated with the low concentration were slightly attacked in Wilhelmshaven. Most of the modified specimens were not infested. Only samples treated with MMF at a concentration of 10 % or with TEOS were moderately attacked. The notional average rating of 0.1 for Belmadur (1.3 M) results from attack by a single animal (Table 2). Interestingly, the type of attack on panels treated with TEOS and MMF differed considerably.

Table 2: Field test results

Wood treatment	Replicates	Notional average rating	
		Hejlsminde	Wilhelmshaven
Accoya	10	0.0	0.0
Belmadur 0.8 M	7	0.0	---
Belmadur 1.3 M	7	0.0	0.1
Belmadur 2.1 M	7	0.0	---
MMF 10 %	10	1.9	2.5
MMF 25 %	10	0.0	---
TEOS	10	1.5	---
Cu Cr 1.2 %	10	0.0	0.8
Cu Cr 5.0 %	10	0.0	0.0
<i>P. sylvestris</i>	10	4.0	4.0
<i>P. radiata</i>	10	4.0	---
<i>P. sylvestris</i> (2009)	5	3.2	2.5

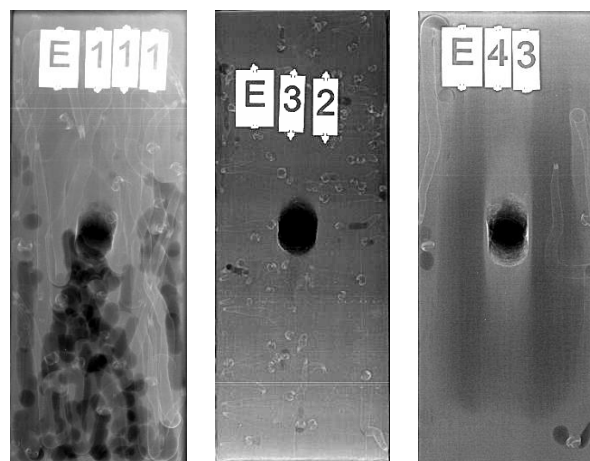


Figure 2: X-rays of an untreated control, a panel treated with TEOS and a panel treated with 10 % MMF

In the first, wood specimens were infested with a high amount of small individuals, while in melamine treated samples few but larger animals could be found (Figure 2). After only two years, the results from the field trial should be regarded as preliminary. It already showed that MMF at 10 % and TEOS only slightly increased resistance to *Teredo navalis*. As a 0.8 molar solution of DMDHEU leads to a higher WPG than 10 % solution of MMF, the results do not allow comparisons of MMF and DMDHEU. While MMF partly penetrates the cell wall (Rapp *et al.* 1999), TEOS only fills the cell lumens when applied in the state of a sol (Donath *et al.* 2004). The different kinds of infestation shown in Figure 2 suggest that cell wall penetration is required to prevent settlement of shipworm larvae, but lumen filling chemicals can slow down the shipworm's growth.

Laboratory assay

Feeding test

In the feeding test, the pellet production rate strongly depended on the material the gribbles fed on (Figure 3). Most pellets were produced from untreated controls. Faster feeding on Radiata pine as compared to Scots pine is probably caused by lower density and hardness of the former. The results for the modifications show a pattern similar to that in the field trial: Pellet production rates are highest on MMF 10 % and TEOS, followed by Belmadur (0.8 M) and MMF (25 %). The animals hardly fed on acetylated wood, sticks treated with higher concentration of DMDHEU and acid copper chromate (Cu Cr). Treatment with a 1.3 M solution of DMDHEU and 25 % of MMF resulted in similar WPGs. Comparing the N-methylol-compounds, DMDHEU performed better in this test. This might be caused by DMDHEU penetrating the cell wall to higher extent than MMF does.

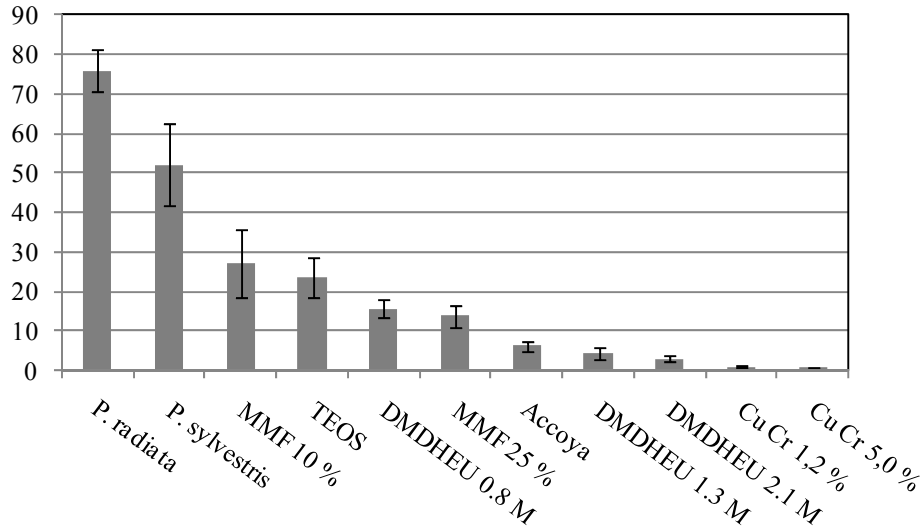


Figure 3: Faecal pellet production by *Limnoria quadripunctata*. (Median \pm 95 % confidence interval).

Choice test

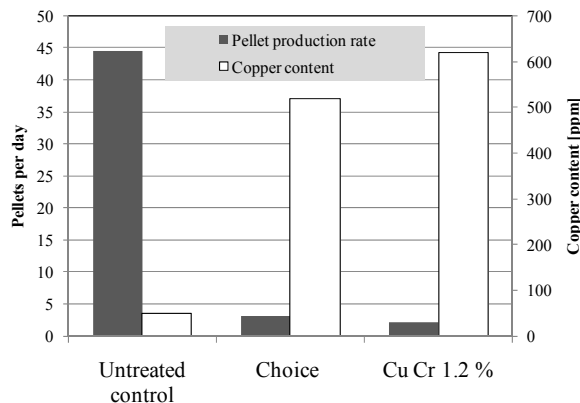


Figure 4: Pellet production rates and copper content in wells containing untreated specimens, specimens treated with acid copper chromate or both.

As expected, the pellet production rates on untreated Scots pine sapwood and copper containing samples were comparable to those found in the feeding test. The amount of pellets produced by animals that were placed in a well with both an untreated and a treated sample was similar to that produced by animals feeding on CC-treated wood alone (Figure 4). Water analysis revealed a high concentration of copper but no chromium. The results of this test suggest that the low pellet production rate on copper containing samples was caused by the toxic effect of leached copper. Thus, conclusions on the resistance of the treated wood in real life situations should not be drawn.

CONCLUSIONS

Modification with thermosetting resins and through acetylation increases the resistance of wood to both gribbles and shipworms. However, minimum WPG and sufficient cell wall penetration are required. TEOS treatment, which fills the lumen with silicate, did not reduce the number of animals boring into the wood, but slowed down their growth.

Although the resistance to different animals was evaluated in the field trial and the laboratory test, similar results were found for the materials tested. This suggests that identical wood properties influence the resistance to both types of borers. For the evaluation of materials with leachable compounds another setup needs to be used in the laboratory test (Borges *et al.* 2008).

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