The Eighth European
Conference on
Wood Modification

ECWM8

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In association with:
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Preface

When we met in 2003 for the final conference of the European Network on Wood Modification, and at the same time celebrated the inaugural ECWM, we planned to meet every 2-3 years to exchange thoughts and knowledge in this new and developing research field. The first conference was very successful and all subsequent ones have been very successful too. ECWM has now evolved into a bi-annual meeting place for international researchers and industry. Participation from outside Europe has been growing and the title of the conference could have been changed to WCWM (World Conference on Wood Modification).

This year we meet in Helsinki. A very good place to meet for a conference on this topic because, since the beginnings of wood modification in Europe in the 1990´s, Finland has been a leading country. Here, the first thermal modification processes were commercialized at larger scale and Finland is still the largest producer of thermally modified wood in Europe and most probably worldwide.

ECWM8 meets just 1.5 years after ECWM 7 and the organizing committee was doubtful if there would be enough interest so soon after the Lisbon meeting. The large number of abstracts sent in suggested just the opposite. The scientific committee had a hard job in selecting papers from the many interesting abstracts submitted and I hope that the resulting program will find your interest. As before, this year's ECWM is linked to the European COST organization. Thanks go to COST Action FP 1303 for strengthening our network!

My special thanks go to the local organizers from Aalto University who have already done a great job in getting us all together in Helsinki and who will certainly make every effort to ensure that we feel comfortable during these days.

Holger Militz

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

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Wood in a sustainable future

Humankind has used wood for millennia, not just as a material for building shelters and other artefacts, but also as a fuel for cooking and for warmth. Wood has been used for so long and is, in many senses, so familiar to us that we rarely, if ever, stop to think about what wood really is. Yet, when we study wood, we begin realise what an extraordinarily complex and elegant material it really is and how it might help us in the creation of a more sustainable future.

With the global challenges of climate change and population growth, there is a very urgent need to reduce our dependence on non-renewable fossil resources and to switch to materials and energy derived from renewable origins. At the same time we need to ensure that the resources we do use, be they renewable or non-renewable, are used parsimoniously. As a renewable and plentiful, though certainly not inexhaustible, raw material wood can help us meet some of these challenges. However, if we are to increase our reliance on wood we must do this with care – we must ensure that we make the best use of our finite resources and ensure that the forests from where we obtain our wood remain healthy – we must "live within our means". Making best use of our resources brings us to the topic of this conference series – the modification of wood.

As we know wood is not without its problems! It has a nasty habit of biodegrading when you least want it to – just add water and it will often happily rot away, acting a food source to a wide variety of micro-organisms. It reacts to changes in its surrounding by altering its dimensions and sometimes shape as well. However, as building material it is in many ways unparalleled and by re-constituting wood in the form of a composite, or though modification, many of its less desirable properties can be wholly or partly eliminated. In the drive to reduce the rate of climate change, the ability of wood to store atmospheric carbon as part of its structure – every kilogram of dry wood requires around 1.75 kilogrammes of (atmospheric) carbon dioxide to create it in the first place – makes it particularly attractive. Long-lasting structures and artefacts built of wood and wood-based composites can therefore store carbon for as long as they exist, which can be for decades or even centuries, and in the end the wood can be burned for energy recovery or, better still, used as the basis for chemicals, or other products – cascaded. Increasing the longevity of wood and extending its utility and function are key topics in the area of wood modification research.

Finland is a country of forests and lakes. It is therefore unsurprising that a vibrant forest-based industry became established here and that many building have been, and are still, built of wood. Indeed there is currently a great deal of interest in building more with wood in Finland and many projects, including an eight storey apartment block, have recently been completed here. Finland is also where the ThermoWood® process was developed, one of the growing number of commercial wood modification processes. We hope that this will make Helsinki a fitting setting for the Eighth European Conference of Wood Modification. Welcome!

The Organising Team

Acknowledgement to COST

COST is an intergovernmental framework for European Cooperation in Science and Technology, allowing the coordination of nationally-funded research on a European level.

COST has a very specific mission and goal. It contributes to reducing the fragmentation in European research investments and opening the European Research Area to cooperation worldwide.

As a precursor of advanced multidisciplinary research, COST plays a very important role in building a European Research Area (ERA). It anticipates and complements the activities of the EU Framework Programmes, constituting a “bridge” towards the scientific communities of emerging countries. It also increases the mobility of researchers across Europe and fosters the establishment of scientific excellence in nine key domains, with Forestry, their Products and Services (FPS) being one of these. At any given time, there are between 20 and 30 COST Actions running within the FPS Domain, each one running for 3-4 years.

As in previous ECWM conferences, ECWM8 has been fortunate to be linked with one of the current COST Actions, **FP1303**: Performance of bio-based building materials

As part of the interaction between this Action and ECWM8, the following presenters have been provided with financial assistance towards travel and subsistence for their involvement at this conference:

Michael Altgen (Germany), Mikos Bak (Hungary), Wilfried Beikircher (Austria), Vladimirs Biziks (Germany), Christian Brischke (Germany), Lothar Clauder (Germany), Simon Cragg (UK), Bruno Esteves (Portugal), Andrzej Fojutowski (Poland), Philippe Gerardin (France), Carolina Greibeler (Spain), Henrik Herajarvi (Finland), Rene Alexander Herrera Diaz (Spain), Callum Hill (UK), Mihar Humar (Slovenia), Dennis Jones (Sweden), Susanna Källbom (Sweden), Andreja Kutnar (Slovenia), Magdalena Kutnik (France), Holger Militz (Germany), Andris Morozovs (Latvia), Marion Noel (Switzerland), Lina Nunes (Portugal), Carmen-Mihaela Popescu (Romania), Rebecka Ringman (Sweden), Anna Sandak (Italy), Kristoffer Segerholm (Sweden), Joris Van Acker (Belgium), Wim Willems (Netherlands) and Vjekoslav Zivkovic (Croatia).

The generous financial awards given to these persons by COST are hereby gratefully acknowledged.

COST 1303 - Foreword

The European Conference on Wood Modification (ECWM) has become established as the foremost conference on the subject, attracting researchers and industry from around the globe. This eighth conference demonstrates the continued interest in all forms of wood modification. The conference provides an ideal platform for academics and industry to discuss the latest developments in product design and manufacture, along with the performance of the material and manufactured products. Increased performance and greater demand from consumers, combined with more stringent environmental regulations provides an excellent opportunity for modified wood to gain increased market share.

In order to help develop and deliver products meeting these ever changing and increased demands from consumers, it is essential for industry to collaborate closely with academia. Such interactions are strongly promoted by the European Cooperation in Science and Technology (COST) networks.

COST is not a new concept – it has been around since 1971. COST was and still is the first and widest European framework for the transnational coordination of nationally funded research activities. It is based on an inter-governmental agreement and comprises currently 36 European Member Countries plus one Cooperating State (Israel). Modified wood has been part of several previous COST Actions including: E2 (Wood Durability), which ran from 1994 to 1999; E22 (Environmental Optimisation of Wood Protection) from 1999 to 2004; E37 (Sustainability Through New Technologies For Enhanced Wood Durability) from 2004 to 2008; and more recently FP0904 (Thermo-Hydro-Mechanical Wood Behaviour and Processing) from 2010 to 2014.

Increasing the understanding and the ways materials behave in service are key activities within COST Action FP1303 “Performance of bio-based building materials”, and these are themes that are well reported within the programme for this year’s ECWM – particularly the sessions on “Moisture Relationship” and “Performance”. Given these common themes, it is logical to develop the link between COST FP1303 and this year’s ECWM. This will allow ECWM and COST FP1303 to collaborate on common themes and help develop new commercial opportunities.

On behalf of COST Action FP1303, I hope you find this joint conference interesting and stimulating, with it providing new links and opportunities.

Dennis

Dennis Jones
Chair, FP1303

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SESSION ONE

Commercial Opportunities for Modified Wood

Trends Impacting Modified Wood Products and the Need for Continued Evolution of Thermally Modified Wood

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ABSTRACT

Rapid development towards urbanization and significant demographic changes are impacting on the future requirements of building products. Increasing demand for defect free, high performance products is favoring the use of mass produced composites often derived from non-renewable materials. Multi family living is becoming the norm with mid to high rise buildings increasing due to lack and cost of prime city land. With the growth in such buildings comes an increased need for higher performance in exterior products with greater importance placed on cost over the life cycle, limited need for maintenance, homogeneous and pleasing appearance, high durability and in many cases fire resistance. Many of these key requirements are extremely challenging for standard wood products to meet and thus there continues to be a growing contradiction between the impacts of global trends and the current technical capabilities of wood based products. Other challenges such as increasing constraints on use of efficient chemicals for durability and protection are making the competiveness of wood products even more challenged.

The evolution of thermally modified wood into the position as the largest wood modification product globally has gone some way to improve the performance of solid wood products without the need for chemical intervention. Extensive research has continued in the field of thermal modification with several technological approaches being developed to achieve similar objectives including atmospheric steam, elevated steam pressure, hot oil and nitrogen atmosphere treatment. The recently completed R&D program commissioned by the International ThermoWood Association aimed to address some of the fundamental factors such as choice of raw material and its suitability to the intended end uses, process steps and conditions, resultant chemical and physical changes and also the effects of alternative process technologies namely atmospheric steam pressure and elevated steam pressure. The research program which was carried out with the University of Göttingen and Mikkeli School of Applied Sciences revealed some interesting results and has created a greater understanding of the critical parameters in producing thermally modified wood. With this new knowledge it is hoped that further development of thermally modified wood can be achieved to meet the growing demands on wood products in the built environment and hopefully faster proliferation of its use.

Wood Modification in Europe in the Year 2015: a Success Story?

Holger Militz

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ABSTRACT

Research on wood modification in Europe has been reported since the 1950´s. However, for political and commercial reasons, the first steps in the commercialization of modified wood in substantial quantities were only taken approximately 20 years ago with the introduction of several heat treatment technologies throughout Europe. Some years later other, new, modification technologies started their production with production sites in e.g. The Netherlands, Norway, Austria and Germany. In 2015, the total production of modified wood in Europe is estimated to be 300.000-400.000 m^3. In a worldwide context this is certainly more than in other part of the world. However, the steps to enlarge market share are small and many challenges, from laboratory to market scale, still have to be overcome. In this keynote, the actual situation is reviewed. The existing processes, products, production capacities etc. are presented and discussed. Up to now, most of the processes have focused on modifying solid wood. Research is now focusing on improving existing, and introducing new, processes. Limited, but growing amounts of modified wood composites are approaching the market. Besides solid wood modification, this keynote will deal with the modification of wood composites, with a focus on veneer modification.

SESSION TWO

Moisture Relationships

Measurement of Dimensional Stability

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Keywords: anti-shrink efficiency, dimensional stability, humidity cycling, test methods

ABSTRACT

Dimensional stability is an important property for wood modifications, but there do not appear to be internationally-recognised standard methods for measuring dimensional stability. There are a number of different underlying mechanisms that can be measured (time based vs. equilibrium tests; liquid water vs water vapour), but even for one type of test, methods tend to vary between different testing facilities, leading to difficulty in comparing results from different studies. Hill (2006) described the international adoption of agreed testing protocols "a matter of great urgency", and we believe that this is still the case. At Scion, we have looked at different test methods that are being used in research at present and have developed and/or adapted several test methods which we have then used for dimensional stability measurement. These have been chosen to mimic a range of in-service stability challenges and thus give results that are applicable to different end uses. Two test methods are outlined here; water-soak/oven dry (to give an Anti-Shrink Efficiency measure, ASE) and long term (equilibrium) humidity cycling.

INTRODUCTION

Most people in wood modification research would agree that dimensional stability is an important wood property, and improved stability is a desired outcome of many wood modifications. Currently a wide variety of tests are used to measure dimensional stability, and even within the same basic test, methods vary considerably between facilities. Anti-Shrink Efficiency (ASE) is a widely reported metric in wood modification research, but test methods used can vary, which makes comparisons between studies difficult.

At Scion, we have been expanding our property testing programme for modified woods, with a particular emphasis on tests that give indications of in-service performance of the wood. We had been measuring ASE for a number of years, but were finding that this metric was not well accepted in industry, because the conditions used (pressure saturation and oven drying) were not representative of conditions the wood would experience in service, so we wanted to extend our testing to include a humidity cycling test. We were unable to find suitable standards for humidity cycling tests, or find consensus in the literature for tests methods for these.

The further we investigated dimensional stability testing, the more we realised that there did not appear to be any accepted standards for ASE determination either. This led us to do some development work of our own, looking at aspects of the test which were likely to influence the results, to determine the best method to use.

Two stability tests were chosen to cover the use of liquid water, and humidity cycling. As there is a lot of variation between test methods, the methods used here have been developed using a combination of existing standards, scoping experiments and professional judgement of which methods will give meaningful results. These tests have been performed with unmodified and modified wood samples, and the results presented here to give examples of the results obtained for each test. For the water-soak/oven-dry test (used to calculate ASE), there are a lot of variations in methods that are likely to influence the results. The effects of the following have been investigated: Resaturation method; oven drying method; volume measurement technique and number of testing cycles.

EXPERIMENTAL

For the ASE and Humidity Cycling experiments, radiata pine (*Pinus radiata* D. Don) boards 100x40mm, 0.6m long were modified with a cell-wall impregnation modification. Unmodified control samples were also used, which were end-matched to the modified boards during sample preparation. During preparation, 20mm ‘reference’ biscuits were cut from between each board. These were included in the ASE testing below. Results from two impregnation modifications with different pre-treatments are presented here (“Treat1” and “Treat2”), along with unmodified control samples, as an illustration.

Water-soak/Oven-dry test

For both the control, and modified boards, two 20mm biscuits (100x40mm cross-section) were cut from near one end of each board. The reference biscuits described above were also included in this test. The inclusion of the control boards, which are compared to their corresponding reference biscuits gives an indication of the degree of scatter present in the results, since the control boards should have an ASE value of zero. This also allows statistical comparisons between the modified boards and unmodified controls.

The biscuits were resaturated using a vacuum-pressure-soak method (Hill, 2006); the samples were submerged in water, vacuum applied for 15 minutes, pressure was applied to 175kPa for 1 hour, followed by atmospheric-pressure soaking for 24 hours (which may not have been long enough to reach weight equilibrium, see method development below). After soaking, the width, thickness and length of the samples were measured with digital calipers. The samples were then dried overnight using a 50/40°C kiln schedule. The samples were then transferred to a laboratory oven, and the samples were dried at 103°C until constant weight. The sample dimensions were measured again. Two further water-soak/oven-dry cycles were completed with these samples. For each cycle anti-shrink efficiency (ASE) was calculated from Equation 1.

$$ASE = \frac{(VC_{WS}-VC_{OD})/VC_{OD}-(VT_{WS}-VT_{OD})/VT_{OD}}{(VC_{WS}-VC_{OD})/VC_{OD}} \times 100 \tag{1}$$

Where:

VC_{WS}	volume of reference sample after water soaking	(mm^3)
VC_{OD}	volume of reference sample after oven drying	(mm^3)
VT_{WS}	volume of treated sample after water soaking	(mm^3)
VT_{OD}	volume of treated sample after oven drying	(mm^3)

Values from each cycle are generally averaged to give an overall ASE result.

Equilibrium Humidity Cycling

This test was based on the European standard DIN 52 184 (1979) where 30x30x10 mm (RxTxL) blocks were cut from each sample to be tested, taking care to align the growth rings in the radial and tangential directions. Wood used for this test must not have been previously oven dried, as this alters the sorption behaviour (Hoffmeyer, *et al*., 2011).
The blocks were placed in a controlled environment at 25°C 65% RH, until constant mass was attained (defined as less than 0.1% change in mass over 24 hours).
The dimensions of the blocks were then measured in the radial and tangential directions, using a bench-mounted dial gauge accurate to 0.001 mm. Measurements were made at a point marked 10mm from one corner of the block. This method enabled accurate and repeatable measurement of the same locations on each block for every measurement, necessary to minimise measurement errors in these comparatively small samples.
After the initial dimension measurement, the samples were cycled through the controlled environments listed in Table 1 until their weight had stabilised, and dimensions were measured again according to the method above. This constitutes one full humidity cycle. Two further humidity cycles were completed, and then the blocks were oven dried at 103°C to constant weight, and the weight and dimensions recorded again.

Table 1: Conditions used for equilibrium humidity cycling

Step	Temperature (°C)	Humidity (%)
1	25°C	60-70% RH (Medium)
2	25°C	90-95% RH (High)
3	25°C	60-70% RH (Medium)
4	25°C	30-40% RH (Low)

From this data, the following calculations can be made for each humidity step.

Radial dimensional change:

$$\Delta R = \frac{R_{MC} - R_{OD}}{R_{OD}} \times 100 \qquad (2)$$

Where:

R_{MC}	radial dimension at the specified humidity	(mm)
R_{OD}	radial dimension when oven dry	(mm)
ΔR	percentage change in radial dimension from oven dry	(%)

Tangential dimensional change (ΔT) is calculated in the same way.

These calculations are relative to oven-dry dimensions, which do not have a lot of relevance to an in-service situation, where the wood will alternate between periods of high and low air humidity, without ever being oven dried. As a more useful measure of the change in dimension, the swelling coefficient h can be calculated. This is defined as the change in dimension for each 1% change in relative humidity. In DIN 52 184, this is calculated from two measurements from different humidity levels, as follows:

$$\boldsymbol{h_R} = \frac{\boldsymbol{R_{MC1} - R_{MC2}}}{\boldsymbol{R_{OD}(RH_{MC1} - RH_{MC2})}} \times 100 \qquad (3)$$

Where:

h_R	Swelling Coefficient in the Radial dimension	
RH_{MC1}	Relative humidity at first measurement level	(%)
RH_{MC2}	Relative humidity at second measurement level	(%)

And all other terms are as defined above.

For each sample 3-6 measurements were taken at each humidity level, so in this work the swelling coefficient is calculated as the slope of a line fitted between the dimensional change values calculated in (2), and the relative humidity level at which they were measured. An example of this is shown in Figure 2.

Water-soak/Oven-dry test – Method development

For these tests, radiata pine boards treated with an impregnation modification were cut into full cross section (100x40mm) biscuits 20mm long.

Resaturation time

Because modifications target the interactions between the wood and water, modified samples may take longer to become fully resaturated, compared to unmodified wood. Modified biscuits were pressure impregnated with deionised water (under 175kPa pressure), and left submerged in water for 48 hours. The sample cross-sectional dimensions (tangential and radial direction) and weights were measured after 1, 24 and 48 hours of immersion.

Oven Drying Method

During the water-soak/oven-dry test, many samples develop cracks after several cycles, and this makes the samples difficult to measure, as they lose strength, and calls into question the applicability of results measured on damaged samples (Hill, et al., 1996). Here two oven drying methods were trialled – kiln drying at 50°C/40°C overnight, then oven drying at 103°C to constant weight; and oven drying for approximately 24 hours until the samples reach a constant weight. After drying, the samples were weighed, their dimensions measured, and the presence or absence of internal checks were observed. This was done for two water-soak/oven-dry cycles.

Number of cycles required

Data from the water-soak/oven-dry test method above was analysed to determine the effect of cycle on the ASE values.

Displacement volume of resaturated samples

Generally the sample volume is calculated by measuring the sample dimensions with calipers. As this involves multiple measurements, and assumes that the sample is perfectly rectangular, there is greater potential for measurement errors, compared to having a single measurement of volume. At Scion, we have been measuring the volume of resaturated samples via water displacement for density determination, and then measuring the sample dimensions to calculate the volume for ASE determination. If these two measurements give equivalent results, then measurement of the resaturated sample volume would simplify the test method, and would decrease the likelihood of measurement errors.

Resaturated biscuits (with 48 hours soaking) had their dimensions (length, width, thickness) measured with 2dp digital calipers and the dimensions in each direction were multiplied together to give the sample volume in mm^3. The sample volume was also measured by water displacement and the displacement weight was multiplied by 1000, to also give a volume in mm^3. Both of these measurements were done for two water-soak/oven-dry cycles.

RESULTS AND DISCUSSION

Anti-Shrink Efficiency (ASE)

Calculated ASE values are shown in Figure 1. Often, if more than one water-soak/oven-dry cycle is performed, data from the first cycle is discarded, so here the results from each cycle are presented separately to show how the results can vary by cycle. ASE values are generally higher in the first cycle, compared to the subsequent cycles, except Treat1 shows much higher and more variable results in the second cycle compared to both the first and third cycles. This effect of cycle number on the ASE values is covered in more detail in the ASE method development section. The ASE results show clear differences between the controls and the modified samples, and the variability of each set of samples is generally lower, suggesting that the modification is not causing variable increases in dimensional stability. The differences between the two modifications are less clear, possibly due to the variability of the results from Treat 1. The control samples are expected to have an ASE of zero, and their average is very close to zero in the second and third cycles, but there is a lot of scatter in the ASE values, showing the high level of uncertainty present in the results.

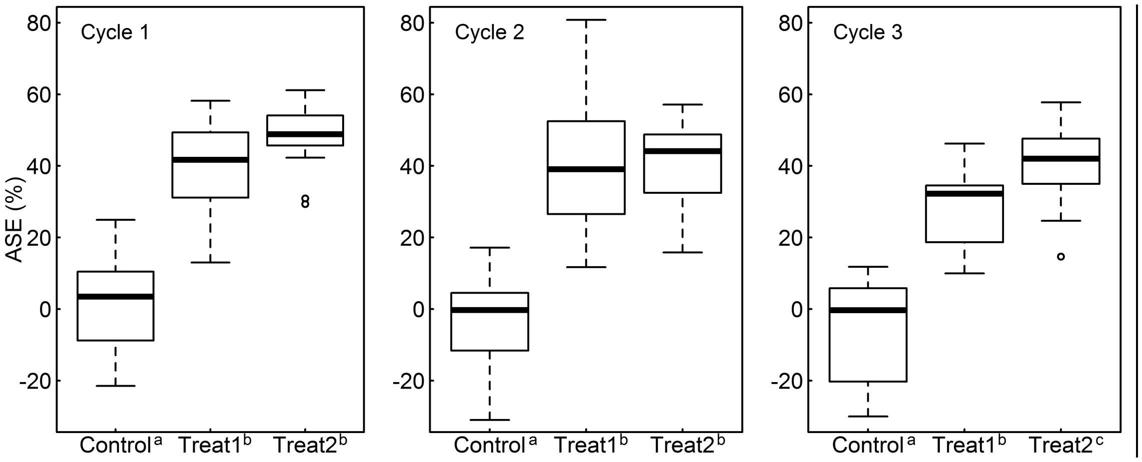

Figure 1: Anti-shrink Efficiency (ASE) for each cycle. Superscript letters indicate treatments that are not significantly different (95% confidence)

Equilibrium Humidity Cycling

Results from the equilibrium humidity cycling test are shown in Figure 2b. The modified samples change dimension less than the unmodified samples. The trends seen here are similar to those of the ASE test, but there is less variability in the results. Compared to the ASE results, the humidity cycling test also gives a result which is easier to relate to the in-service performance of the modified wood. One example of the line fitted to calculate the change in dimension with changes in humidity is shown in Figure 2a. The change in dimension is linear with relative humidity, so the fitted line is representative of the behaviour over the entire humidity range measured. It can be seen that the dimensions of the sample tended to decrease with subsequent cycles and this was true of the majority of the samples. It was expected that the first cycle would be different from subsequent cycles, but this behaviour has continued into the second humidity cycle, suggesting that more than three cycles may be needed to get representative data. Equilibrium humidity cycling is a very time consuming test, taking many weeks, compared to the water–soak/oven-dry test which can be completed in a matter of days. Ensuring sufficient humidity cycles are performed will make this test even more time consuming.

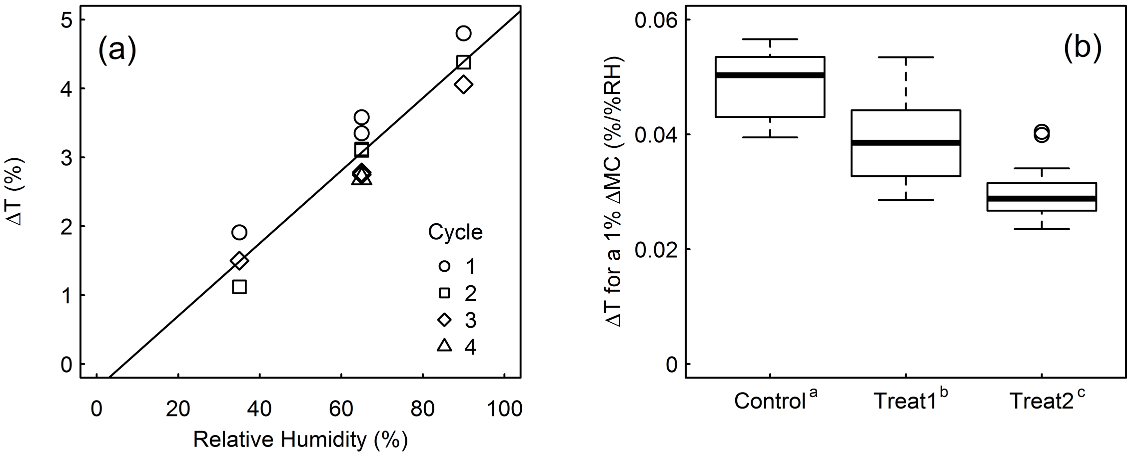

Figure 2: Example of a fitted line for one representative sample (a) and change in tangential dimensions with a 1% change in atmospheric humidity (b). Superscript letters indicate treatments that are not significantly different (95% confidence)

Water-soak/Oven-dry Test Method Development

Resaturation time

The average weights and dimensions of the biscuits at each measurement time are shown in Table 2. Significance letters indicate treatments that are significantly different to each other at the 95% confidence interval, using paired comparisons to compare successive measurements on each individual biscuit. As can be seen, the 48 hour resaturation time corresponds to increased sample weight, and increased tangential dimensions compared to both the 1 and 24 hour resaturation times. From these values, at least a 48 hour soaking following resaturation is recommended for this size of biscuit. Other biscuit sizes may need to soak even longer. Monitoring the sample weights, as is done for the oven drying method below, would ensure complete saturation had been reached.

Table 2. Weights and dimensions of biscuits during resaturation. Letters indicate values that are not significantly different at the 95% confidence level.

Resaturation time (h)	Weight (g)	Radial (mm)	Tangential (mm)
1	51.5 ^{a}	39.4 ^{a}	100.7 ^{a}
24	53.5 ^{b}	39.4 ^{a}	100.8 ^{b}
48	56.7 ^{c}	39.4 ^{a}	101.0 ^{c}

Oven Drying Method

For the samples kiln dried prior to oven drying, 5% had checks by the second cycle, and for the oven dried samples, 27% were checked, with unmodified biscuits appearing to have more checks than the modified biscuits. A chi-squared independence test shows that the difference in the overall proportion of boards checked is significant (95% confidence: $c^2(2, N = 64) = 3.408, p < 0.01$), suggesting that the initial kiln drying step can be used to reduce the incidence of checking in the biscuits during testing.

Number of Cycles

The ASE values of each sample were compared between the three cycles using a pairwise t-test. This showed that the ASE values between cycles 1 and 3 were significantly different (p <0.001), but neither were significant to cycle 2 (p =0.027). As can be seen in Figure 1, ASE values in cycle 1 tend to be somewhat higher to those in the subsequent two cycles, and for Treat1 the results from cycle 2 were very different, and very variable compared to the other cycles. From this, it is recommended that three or more water-soak/oven-dry cycles are used, and that data from the first cycle is discarded.

Displacement volume of resaturated samples

In Figure 3 the displacement volume measured in cycle 1 is plotted against that measured in cycle 2. The two measurements are highly correlated (r^2 = 0.976, p <0.001) and the slope of the best fit line is 0.99, so overall the two measurements are giving very similar values.

Because the displacement volume measurement only requires one measurement to be taken, compared to three or more for the dimension volume, the displacement volume measurements might be expected to have less variability due to measurement errors, compared to the dimension measurements. A plot of the volumes calculated in cycle 1 against those of cycle 2 will highlight any major differences in volume, which would likely be caused by measurement error. This can be seen in Figure 3.

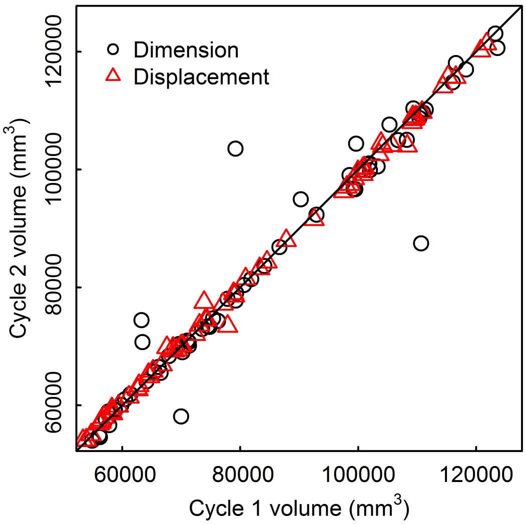

Figure 3: Correlation between cycle 1 and cycle 2 volumes for each measurement type. The solid line indicates the relationship Cycle 2 volume = Cycle 1 volume

Both measurements tend to fall around the equivalence line, showing that the volumes are very similar cycle-to-cycle, but the volume measured by dimension does have some notable outliers, where the volumes vary substantially between cycles. This is not seen for the data measured by displacement, which, it should be remembered, was measured on the same samples, at the same time, so differences between the measurement methods are likely to be due to measurement error. Therefore it is recommended that the water-saturated volume of test samples be measured by displacement in water, rather than by measuring dimensions with calipers.

CONCLUSIONS

Finding suitable, commonly-used tests for measuring dimensional stability can be difficult, especially for humidity cycling tests. At Scion we have been adapting existing test methods to create tests that will give meaningful repeatable results, which give good indications of the performance of modified wood in service. A water soak test, and a humidity cycling test have been outlined, along with method development that has gone into refining these methods to make sure we get meaningful test results.

We are hoping that this development work will lead to a wider discussion on dimensional stability measurement methods, and how these might be standardised.

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Effect of Prolonged Water Soaking on Structure and Chemistry of Thermally Modified Scots Pine and Norway Spruce Wood

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Keywords: anatomy, chemistry, hardness, pH, thermal modification

ABSTRACT

Changes in structure and chemistry of thermally modified wood applied in water contact conditions are considerable challenges for the use of thermally modified wood in the outdoor constructions. Therefore, the structure and chemical components of cell wall of thermally modified Scots pine (*Pinus sylvestris* L.) and Norway spruce (*Picea abies* Karst.) under prolonged water soaking were investigated in this research. Thermally modified Scots pine and Norway spruce specimens with two thermal treatment classes (Thermo-S® and Thermo-D®) and two thicknesses (25 and 50 mm) were soaked in tap water in room temperature for approximately 20 weeks. Changes in anatomical structure, Pilodyn hardness, water absorption, pH and surface chemistry were analysed in every two weeks. The results were compared with untreated control specimens prepared from both species. Soaking induced slightly faster deterioration in thermally modified pine than in control specimens. After reaching the fibre saturation point in approximately two weeks of soaking, the Pilodyn hardness of thermally modified specimens started a slow but steady decrease. Modified specimens absorbed water slower than the control specimens. Initial pH value of thermally modified specimens was lower than that of control specimens, but no change in pH was observed during the soaking period. The FTIR spectroscopy results indicate degradation of polysaccharides probably due to the hydrolysis during soaking. Those changes indicate degradation in both physical and chemical properties of thermally modified Scots pine and Norway spruce in prolonged water exposure.

INTRODUCTION

Thermal modification has been employed as an industrial method for wood preservation for approximately 20 years. Five main commercial methods for the thermal modification of wood have been developed in Finland, Germany, the Netherlands, and France. All of these processes treat wood with temperatures between 160 and 240 °C but differences arise from the raw materials used, processes, heating media and equipment used (*e.g.,* Esteves and Pereira 2009, Boonstra 2008).

Large chemical changes occur during thermal modification, including degradation of hemicelluloses, generation of acetic acid, increase of crystallinity, depolymerization of cellulose, and crosslink reaction of lignin (Tjeerdsma *et al.* 1998, Yildiz *et al.* 2006, Gonzalez-Pena *et al.* 2009). As a consequence, wood loses its mass, cracks and porosity in cell walls occur, and physical properties are also changed (Fengel and Wegener 1989, Andersson *et al.* 2005). The higher is the treatment temperature and the longer is its duration, the more obvious are the changes. In addition, after thermal modification wood components are degraded, equilibrium moisture content is reduced, mechanical properties are changed, and the dimensional stability and fungal resistance are enhanced (Hillis 1984, Kamdem *et al.* 2002, Weiland and Guyonnet 2003, Shi *et al.* 2007, Korkut *et al.* 2008, Borrega *et al*. 2009, Heräjärvi 2009).

Most wood species are known to be acidic in neutral situation. Thus acidic hydrolysis of wood components happens when water is present (Fengel and Wegener 1989, Sundqvist 2004). Furthermore, acidic hydrolysis of wood will be accelerated by other organic acids generated during thermal modification, which leads to the degradation of polysaccharides into component sugar molecules by the cleavage of glycosidic bonds (Tjeerdsma *et al.* 1998).

The aim of this research was to investigate the key phenomena behind thermally modified Scots pine and Norway spruce in long-term water exposure condition.

EXPERIMENTAL

Materials

Wood materials used in this study were thermally modified Scots pine and Norway spruce boards with mixed sapwood and heartwood, obtained from industrial processes of member companies of International Thermowood® Association. The sizes of specimens were 25 and 50 *100*215 mm (T*W*L). Two thermal modifications were applied for both species: Thermo-S® (treatment parameter 180 °C/2h) and Thermo-D® (212 °C/3h for 25 mm thick, 212°C/4h for 50 mm thick). Untreated specimens prepared from both species were used as control.

Specimens for different measurements were soaked in separate buckets filled with tap water and stored in room temperature. Water was changed once a week for the first eight weeks. After that, water was changed after each two weeks.

Anatomical observations

Anatomical changes were observed using a reverse light microscope Nikon Eclipse MA200 at magnification of 50 times. Altogether 13 microtomed specimens, representing only Thermo-D® Scots pine, were used. Ten of the specimens represented thermally modified wood and three represented control.

Pilodyn hardness measurement and water absorption analysis

Pilodyn hardness was measured from the pith-side surface of specimens by Pilodyn penetrometer (Pilodyn 6J, Proceq Corp.). The force of Pilodyn was set at 30 N. The pin with 2.55 mm diameter penetrated into wood with 30 degree angle. High Pilodyn value refers to low hardness. Every specimen was measured three times at different positions in each measurement.

Water absorption rate was measured as mass change from the Pilodyn hardness specimens.

pH measurement

Specimens with drilled holes (diameter: 16.5±0.3 mm, depth: 23±1 mm) on pith-side surface were prepared before soaking. During each measurement, de-ionized water (ultra pure (type 1) Milli-Q water) was filled into the drilled holes, and pH values were measured from the liquid in holes by lab pH meter (PHM 220, MeterLab, Radiometer Analytical Corp.). Each specimen was measured twice in each measurement time. Milli-Q water was changed for the second measurement.

In order to verify the pH result, four specimens were selected to be measured again using the traditional method, which measures pH from wood powder solution. Differences between the results of the two methods were evaluated.

Surface chemistry measurement (FTIR measurement)

Approximately 5-mm-thick pieces were sawn from the specimens for the FTIR measurements before each FTIR measurement time. These pieces were dried at 103±2 °C for 24 hours, and stored in a desiccator. The FTIR spectra were acquired from pith side surface of specimens by FTIR-ATR (Platinum ATR, Bruker Corp.). The scanning range was 400-4000 cm^{-1}, and 16 scans were accumulated at 4 cm^{-1} resolution. All the spectra were baseline corrected at 3670, 3015, 2500, 1900, 1830, 1540, 1396, 1300, 1189 and 838 cm^{-1}, and normalised at 1369 cm^{-1}.

To study the wood property changes as a function of time, the soaking test lasted 5 months, and each measurement was carried out every two weeks. Summary of the general characteristics of the study material is presented in Table 1.

Table 1: Basic density and numbers of specimens in different measurements

	Scots pine						**Norway spruce**					
	25 mm			50 mm			25 mm			50 mm		
	Treatment*											
	S	D	C	S	D	C	S	D	C	S	D	C
Basic density [kg/m^3]**	389	386	-	403	372	376	340	352	-	365	379	351
	Number of specimens in tests											
Anatomy	-	10	3	-	-	-	-	-	-	-	-	-
pH	-	-	-	8	8	4	-	-	-	8	8	4
Pilodyn	-	-	-	14	16	4	-	-	-	11	11	6
Water absorption	16	18	7	14	16	4	16	18	2	11	11	6
FTIR	10	10	6	10	10	5	10	10	2	10	10	10

** Treatments: S=Thermo-S®; D=Thermo-D®; C=untreated control.*
*** Calculated from the original heat treated boards.*

Differences in the mean values of measured variables were analysed by using General Linear Model (GLM) multivariate procedure. The differences in variance of Pilodyn hardness, water absorption and pH results for each date were compared to each other with Levene's test of variance.

RESULTS AND DISCUSSION

Anatomical changes

The changes in cell wall structure of Scots pine due to water soaking treatment are shown in Figure 1. Thermal modification increased the porosity of cell walls. As a result of water contact, size and number of pores increased, particularly in cell walls outer parts. Effects on wood structure occurred earlier and more severe in thermally modified wood than untreated wood, which is most likely due to the acids formed during thermal modification, and promoting acidic hydrolysis of modified wood (Tjeerdsma *et al.* 1998).

Hyphae growth was noticed in all soaked specimens, but less on untreated specimens compared with thermally modified ones. This is obviously due to sugars formed by degradation of wood components.

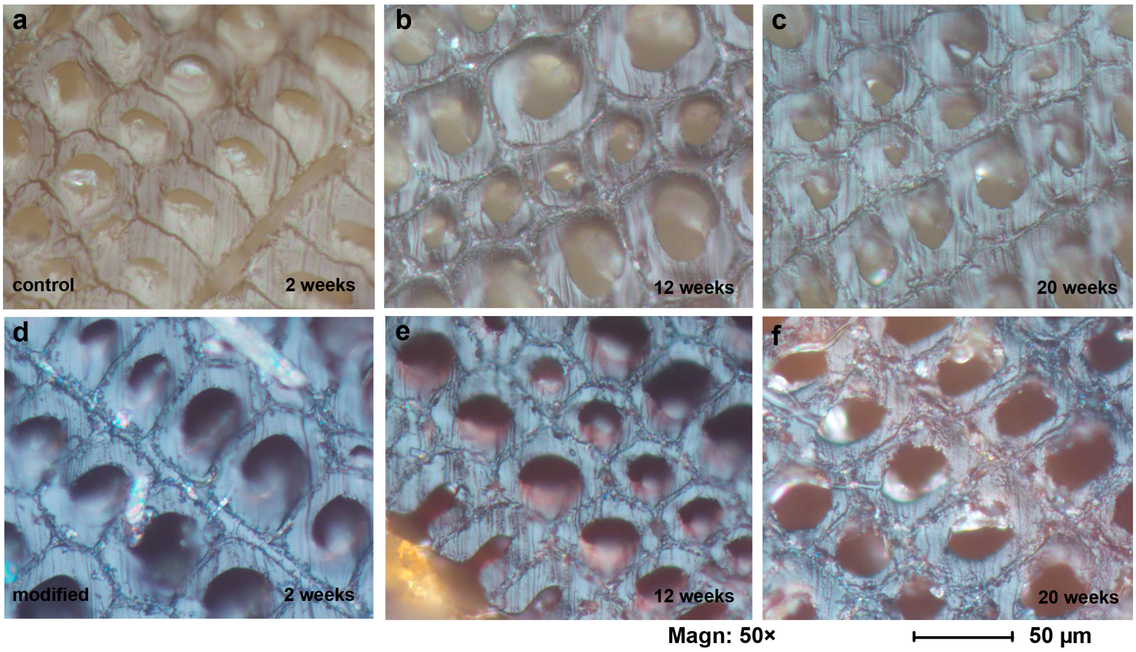

Figure 1: Degradation of cell structure of Scots pine in different soaking periods (a,b,c refer to untreated control specimen;, d,e,f refer to thermally modified specimens)

Pilodyn hardness

Thermal modification decreased the hardness of wood, and dry Thermo-D® wood had lower hardness than dry Thermo-S® wood for both Scots pine and Norway spruce (Figure 2). This result can be related to the more severe deterioration of cell wall and mass loss of wood during thermal modification in higher temperatures (Korkut *et al.* 2008, Salca and Hiziroglu 2014). However, hardness of Thermo-S® and Thermo-D® specimens decreased similarly during soaking.

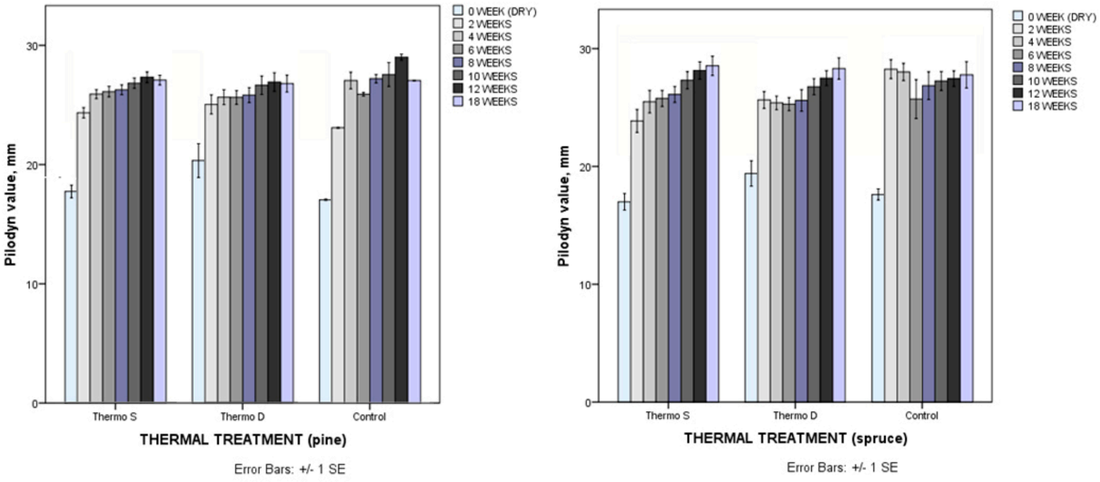

Figure 2: Pilodyn hardness of Scots pine and Norway spruce during soaking time

Before reaching the fibre saturation point (FSP) in approximately two weeks of soaking, hardness of all specimens decreased significantly. According to previous literature, basic density is strongly correlated with hardness (*e.g.,* Heräjärvi 2004, Ponneth *et al.*

2014). Thus, before reaching the FSP, decrease in basic density due to swelling effect is considered to be the main factor affecting hardness.

After two weeks of soaking, the slow but steady decrease in Pilodyn hardness of thermally modified specimens indicated that the deterioration of cellular structure is the main factor that affects hardness.

Water absorption

The water absorption of specimens reflected by the moisture contents during soaking test is presented in Figures 3 and 4.

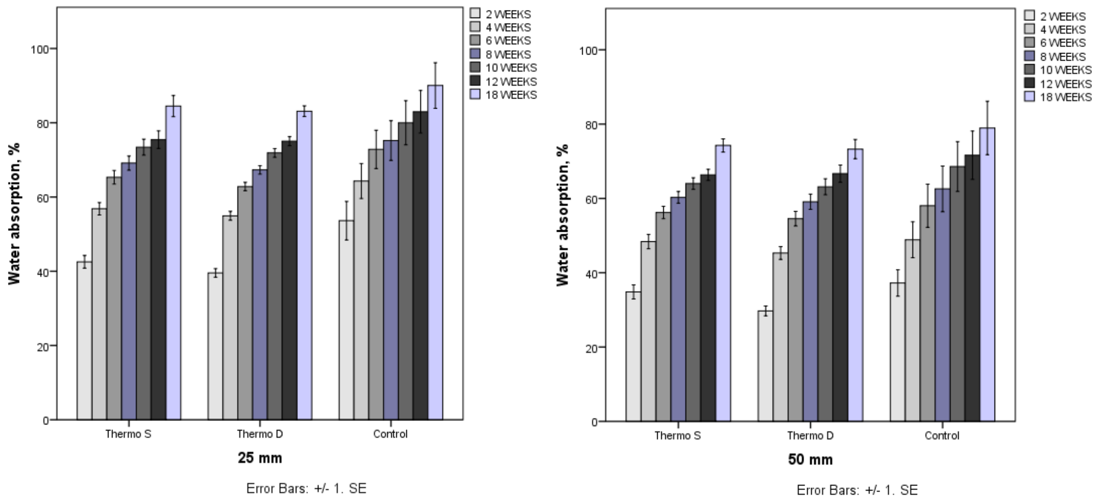

Figure 3: Water absorption of 25 mm and 50 mm thick thermally modified Scots pine specimens (note that the last bar represents 18 weeks of soaking)

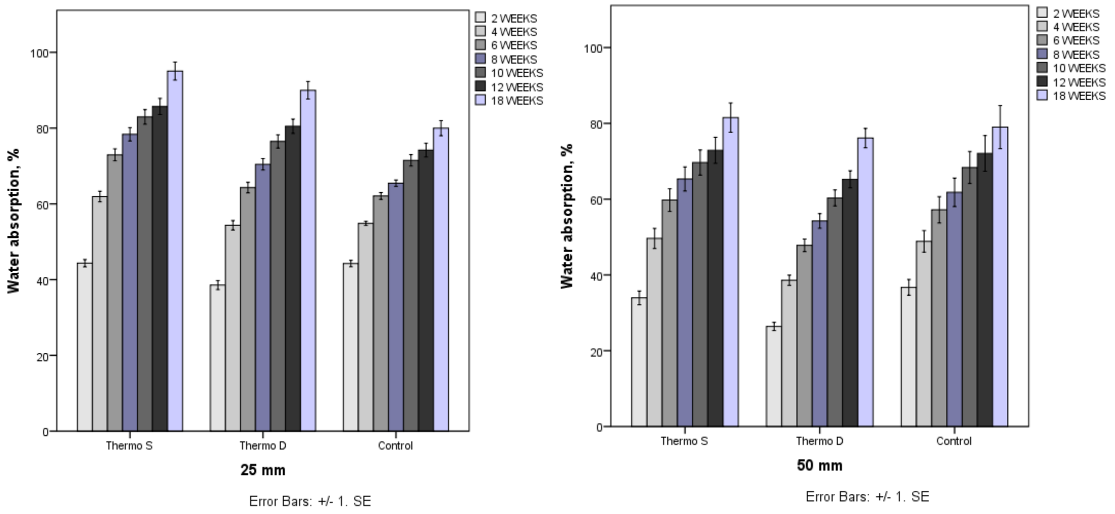

Figure 4: Water absorption of 25 mm and 50 mm thick thermally modified Norway spruce specimens

The water absorption decreased in thermally modified wood with increasing treatment intensity. Thermal modification decreases hydrophilic hydroxyl groups with dehydration reactions, increases cellulose crystallinity, and also leads to the cross-link reaction of lignin (Tjeerdsma *et al.* 1998, Boonstra and Tjeerdsma 2006). Therefore, water molecules are less accessible to thermally modified wood. The water absorbed during soaking is probably due to stress releasing in modified wood after degradation of hemicelluloses and lignin (Kamdem *et al.* 2002).

In case of Norway spruce, Thermo-D® specimens had lower water absorption than Thermo-S® during the entire soaking period. Such difference was not observed between Thermo-S® and Thermo-D® pine. According to Metsä-Kortelainen *et al.* (2006), thermal modification decreases the water absorption of spruce proportionally to the treatment temperature between 170 to 210 °C. In case of Scots pine heartwood the logic is the same, whereas Scots pine sapwood behaves in opposite manner. Since the materials used in this study were mixed sapwood and heartwood, such dependency could not be observed and verified.

pH changes

The pH results indicated no major changes in wood acidity as a result of water soaking. The pH values of thermally modified specimens varied between 4.1 and 4.7, whereas the control specimens' pH was above 5 (Figure 5), indicating the generation of acids from the degradation of hemicelluloses by thermal modification.

Thermo-D® had significantly higher pH than Thermo-S® specimens for both species. In addition, the differences between the two treatments were more obvious for pine than for spruce wood.

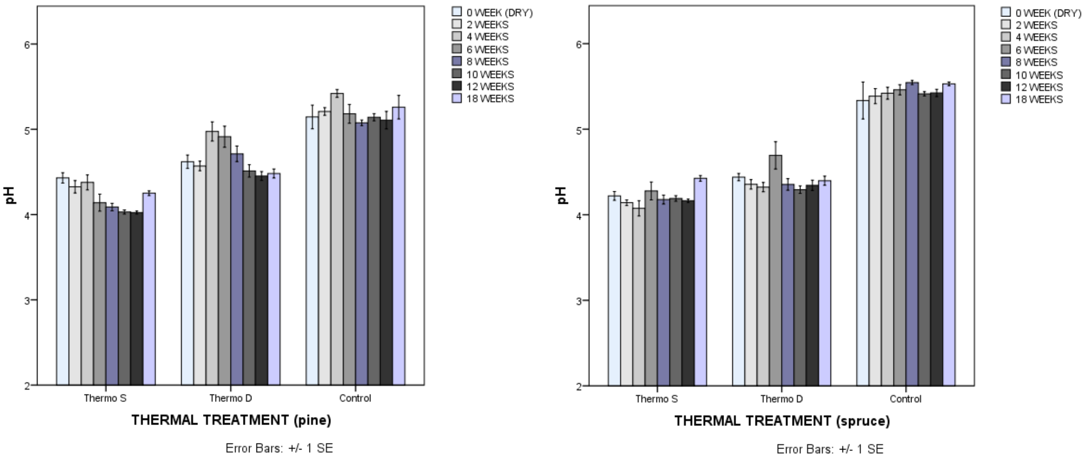

Figure 5. pH value of thermally modified pine and spruce with their controls

After reaching its highest value at approximately 4 weeks of soaking, the pH of thermally modified Scots pine specimens decreased only a little as a function of soaking time, the slow decrease possibly indicated mild acidic hydrolysis, which was not, however, seen in case of pine control and spruce specimens. Changes during the entire soaking period were statistically insignificant.

The average difference of pH values measured by the two methods was 0.22. This difference is considerably big in comparison to the magnitude of changes caused by soaking. Therefore, the occurrence of acidic hydrolysis during this soaking test cannot be confirmed by pH measurement.

Surface chemistry changes

The FTIR spectra confirmed the degradation of hemicelluloses during soaking, being indicated by decreased intensity of C=O stretching in hemicelluloses at 1729 cm^{-1}. The increased signal of aromatic C=O stretching at 1652 cm^{-1} and decreased intensity of guaiacyl-ring features at 1456 cm^{-1} in lignin represent the degradation of lignin and formation of new lignin aromatic structures as a result of hydrolysis. Increase in C=C/C=O structure in cellulose at 1031, 1054, 1103 cm^{-1} indicates modification of cellulose's linkages during soaking.

CONCLUSIONS

The results of this study reveal that microstructure, mechanical performance and chemistry of thermally modified Scots pine and Norway spruce wood suffer to some extent from prolonged water soaking, possibly indicating the phenomenon of acidic hydrolysis. Anatomical changes indicated more severe deterioration in thermally modified than untreated wood. Pilodyn hardness decreased steadily as a function of soaking time, but the treatment parameters do not considerably affect the hardness. Though no significant change was detected by pH test, the results of FTIR indicated that cell wall components were degraded and modified due to soaking effect.

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The Role of Chemical Transport in the Decay Resistance of Modified Wood

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ABSTRACT

A 2014 review by Ringman *et al.* examined established theories addressing why modified wood has increased decay resistance and concluded that the most probable cause of inhibition and/or delay of the initiation of brown rot decay is lowering the equilibrium moisture content for given environmental conditions. A 2013 paper by Jakes *et al.* examined moisture induced wood damage mechanisms that do not appear in dry wood but have onsets at moisture contents below fibre saturation, including wood decay and fastener corrosion, and observed that these damage mechanisms require chemical transport through wood cell walls. They proposed the mechanism for chemical transport within the wood cell walls was controlled by a moisture induced glass transition in interconnected networks of hemicelluloses and amorphous cellulose. Here we show how these models jointly suggest a mechanism by which wood modifications can inhibit brown rot. Alternative mechanisms are also discussed. These models can be used to understand the performance of modified wood and in the development of new modification systems.

INTRODUCTION

As a building material, wood is unique in that it is a completely renewable resource that can sequester carbon during the life of the building (Falk 2009). Furthermore, wood has an excellent strength to weight ratio and is frequently cited as having a warm, pleasing, appearance (Rice *et al.* 2006). However, the interaction of wood with moisture can cause a host of undesirable consequences that, in-part, limit the usefulness of wood as a building material. When the moisture content within the wood is sufficiently high, it is susceptible to biotic attack and becomes corrosive towards embedded metal fasteners. Furthermore, repeated large changes in the hygroscopic range of wood moisture content cause dimensional instability, which can lead to the formation of splits and checks within the wood and failures at wood-adhesive bond lines. When non-durable wood and wood-based products are selected for an application where it will become repeatedly wet in-service, preservative (biocidal) treatments are frequently specified. These treatments protect the wood by excluding fungi or insects that attack the wood through repellent, biostatic, or biocidal actions. However, almost all preservative treatments are regulated pesticides, and their use and availability is subject to their ability to maintain their regulation (Lebow 2004). Over the last 50+ years, wood modifications have been developed as a potential alternative to preservative treatments for use when wood will be exposed to damp conditions.

In contrast to preservative treated wood, where biocidal chemicals (mainly heavy metals) are injected into the wood, wood modification changes the wood structure through a chemical, thermal, or thermochemical process to make it less susceptible to degradation. Common wood modification methods include acetylation, furfurylation, cross-linking agents, such as dimethylol dihydroxyethyleneurea (DMDHEU), and several variations of thermal modifications. All of these modifications have been shown to improve the dimensionally stability and the decay resistance of wood. However, there are differences between the treatments in their ability to resist decay (Temiz *et al.* 2006, Rowell *et al.* 2009, Lande *et al.* 2004, Thybring 2013, Verma *et al.* 2009). Several possible mechanisms have been proposed for how wood modifications protect wood (Boonstra *et al.* 2007, Boonstra and Tjeerdsma 2006, Rowell *et al.* 2009, Rowell 2005, Hill *et al.* 2005, Papadopoulos and Hill 2002). Testing these mechanisms and identifying how wood modifications enhance durability are the keys to finding the preferred uses for modified wood as well as refining the modification techniques for optimum performance and cost.

Here we review recent advances in the understanding of brown rot decay in modified wood and a new model for chemical transport in wood. We then discuss potential mechanisms by which decay resistance occurs in modified wood in light of these recent advances. With each potential mechanism, we clearly highlight testable hypotheses so that future work can test these hypotheses. Finally, the paper highlights the most crucial open questions that can be used to determine the mechanisms resulting in the decay resistance of modified wood.

BROWN ROT DECAY RESISTANCE IN MODIFIED WOOD

Brown-rot decay is characterised by significant reductions in strength even at low mass loss. The brown rot degradation process is divided into two parts: i) chelator-mediated Fenton (CMF) degradation, in which hydroxyl radicals depolymerise polysaccharides in addition to modifying lignin, and ii) enzymatic degradation, in which cellulases and hemicellulases hydrolyse the polysaccharides (Goodell *et al.* 1997, Baldrian and Valášková 2008, Arantes *et al.* 2012). Ringman *et al.* (2014) recently conducted a review of theories of how modification imparts decay resistance to wood and presented four different potential mechanisms:

1. There may not be enough easily accessible nutrients, such as hemicelluloses, in the modified wood material to provide energy for initial degradation, since hemicelluloses are degraded or heavily modified in e.g. thermally modified and acetylated wood (Rowell *et al.* 2009, Boonstra *et al.* 2007). It has also been argued that e.g. arabinose is the trigger of wood degradation (Rowell *et al.* 2009). However, Ringman *et al.* pointed out that celluloses and hemicelluloses are degraded by the same mechanisms so if there are no hemicelluloses, the fungi would most probably degrade cellulose instead. Furthermore, this mechanism would not inhibit CMF degradation.
2. The fungal metabolism process may be disrupted by wood modification through modification of the wood polymers so they are unable to be broken down by fungal enzymes (Rowell, 2005). This mechanism also seems unlikely

to be solely responsible for the enhanced durability of modified wood since brown rot fungi are able to break down wood through CMF degradation.

3. Wood modification may close micropores in the wood cell wall preventing enzymes entering the cell wall. However, Hill *et al*. (2005) showed that for acetylated wood, the entire size range of micropores is accessible to CMF degradation agents in highly modified wood even though the total volume of micropores has decreased.
4. Diffusion of fungal CMF degradation agents may be inhibited since wood modification reduces the equilibrium moisture content by decreasing the free volume within the cell wall (Papadopoulos and Hill 2002, Boonstra and Tjeerdsma 2006). Taking the brown rot degradation process into account, Ringman *et al*. (2014) concludes that out of the four established theories, this is the most plausible one. However, mechanisms 2 and 3 may reduce the rate of the enzymatic breakdown.

We next focus on the relationship between wood moisture content and intra-cell-wall diffusion to show how wood modifications may inhibit diffusion at a given moisture content and how by reducing the moisture content generally, there is a reduction in diffusion.

CHEMICAL TRANSPORT IN WOOD CELL WALLS

A mechanism recently proposed to control the onset of decay in wood was the percolation of rubbery regions in hemicelluloses and amorphous cellulose networks that facilitate the necessary transport of CMF degradation chemicals through wood cell walls (Jakes *et al*. 2013). This onset mechanism was developed based on the observations in the literature that:

1. CMF degradation chemical transport must occur through wood cell walls because the onset 20-25% moisture content for wood decay is below fibre saturation (Griffin 1977, Carll and Highley 1999, Viitanen and Paajanen 1988), suggesting free water is not readily present in the wood structure to facilitate chemical transport
2. Hemicelluloses and amorphous cellulose are proposed to form interconnected networks in wood cell walls. In secondary wood cell walls, amorphous cellulose is found within cellulose microfibrils. Glucomannan is mechanically associated with cellulose microfibrils (Åkerholm and Salmén 2001) and may create a sheath around the microfibril (Terashima *et al.* 2009) or even be present within a microfibril (Salmén and Fahlen 2006). Additionally, xylan forms networks both parallel (Stevanic and Salmén 2009) and perpendicular (Terashima *et al.* 2009) to the cellulose microfibrils in secondary wood cell walls. Hemicelluloses are also embedded as an irregular, interconnected network in lignin to form the middle lamella (Hafren *et al*. 2000).
3. The moisture-induced glass transition of hemicelluloses occurs at lower moisture content than wood decay. The range assessed using mechanical spectroscopy is between 60-80% relative humidity (Kelley *et al.* 1987, Cousins 1978, Olsson and Salmén 2004) at room temperature, which corresponds approximately with 11-15% wood moisture content (MC).
4. Ionic conduction in polymers is much higher in the rubbery state above their glass transition than in the glassy state below their glass transition (Ferry 1980).
5. Ionic conduction in wood as a function of moisture content can be fit with a percolation threshold at 16% moisture content (Zelinka *et al.* 2008).

A schematic of the proposed formation of percolated regions of softened hemicelluloses in the secondary cell wall and middle lamella of two adjacent cell walls is shown in Figure 1. An experiment to test the proposed mechanism and effects of moisture on ionic diffusion in wood cell walls was recently developed using synchrotron-based X-ray fluorescence microscopy (Zelinka *et al.* 2015). In these experiments, a sharp concentration gradient of ions was implanted into thin sections of wood and the relative humidity controlled *in situ* during imaging to allow the observation of humidity thresholds for ion diffusion. It was observed that the threshold moisture content for observable diffusion depended on the ion (Cu, Zn, K, or Cl), cell wall layer (S2 or middle lamella), and orientation (longitudinal or. transverse). The threshold for diffusion was found to be as low as 60% RH for K and Cl ions and potentially be as high as 90% RH for Zn ions in the longitudinal direction. This range of humidity corresponds to the proposed 60-80% RH range for the hemicelluloses passing through their moisture-induced glass transition, supporting the theory that percolated networks of rubbery hemicelluloses and amorphous cellulose could be responsible for ion transport through wood cell walls. Additionally, for all experiments a low RH bound was observed over which no ion diffusion could be observed during the experiment (~10 minutes). The difference in onset RH for different ions might relate to size requirements to the diffusion pathways in the percolated network.

The moisture content threshold of the hemicelluloses glass transition observed using mechanical spectroscopy and ion movement in the XFM experiments may not be the same as the onset moisture content for wood decay. It could be that the CMF degradation chemicals require a different moisture threshold for transport through wood cell walls. Or the time scale of the XFM experiments may be different than the relevant time scales in chemical transport in wood decay. Nevertheless, if the relationship between the moisture threshold of ion diffusion in wood cell walls observed with XFM and onset moisture for wood decay can be further substantiated, the XFM experiments would be a valuable to tool to directly predict the efficacy of a wood treatment on decay resistance.

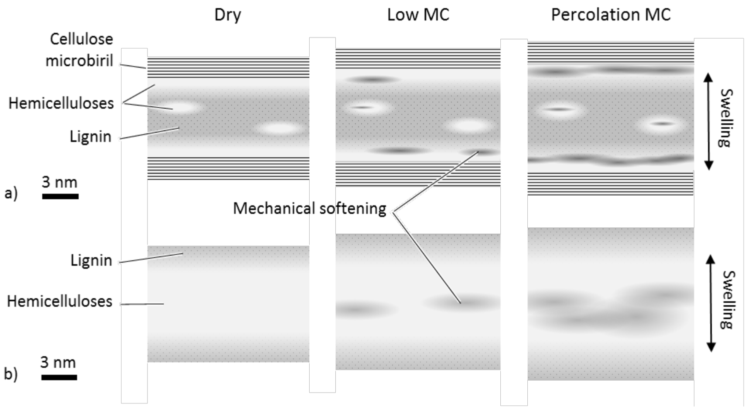

Figure 1: Mechanism of transport proposed by Jakes et al. where transport occurs in interconnected regions of softened hemicelluloses in the (a) S2 layer and (b) middle lamella

DISCUSSION- POTENTIAL MECHANISMS OF DECAY RESISTANCE IN MODIFIED WOOD BASED UPON TRANSPORT THEORIES

In this section we present potential mechanisms by which wood modifications may result in decay resistant wood based upon the recent advances in understanding of brown rot decay and chemical transport in wood presented earlier. Even with these recent advances, there is not yet enough information to know the exact mechanism. Therefore, we present three potential mechanisms by which modified wood may inhibit brown rot decay. Along with each mechanism, we present testable hypotheses; experiments that can prove or disprove each of these mechanisms.

Transport of fungal CMF degradation agents is inhibited by preventing softening of the hemicelluloses

The percolation model of Zelinka *et al*. (2008) and extended transport model of Jakes *et al*. (2013) both suggest that a threshold moisture content exists below which diffusion of at least some chemical species does not occur. One possible mechanism for the decay resistance of modified wood is that diffusion of CMF degradation compounds are inhibited because the percolation threshold has not been reached. In this case, a percolating network would not be achieved because the hemicelluloses remain in their glass state.

Mechanism of decay resistance

This mechanism provides decay resistance by inhibiting the transport of CMF degradation compounds. Chemical modifications that increase the humidity required for hemicelluloses to pass through a glass transition should improve decay resistance. A modification that prevents a hemicellulose glass transition under water saturated conditions should be an effective wood protection treatment because the initial CMF degradation mechanisms are prevented.

Testable hypotheses of this mechanism

If decay resistance was imparted by inhibiting diffusion by stopping the moisture induced glass transition of the hemicelluoses, then there would be no observable diffusion at high moisture contents and the hemicelluloses would be stiffer than in untreated wood at high moisture contents. Previously, XFM was used to examine the diffusion thresholds for unmodified wood (Zelinka *et al.* 2015); this work could be extended to study whether the threshold moisture content changes in modified wood. Furthermore, *in-situ* measurements of the glass transition temperature of hemicelluloses in unmodified and modified wood across a range of moisture contents could determine if the glass transition moisture content tracked with the diffusion threshold.

Transport of fungal CMF degradation agents is inhibited by preventing percolation

Another possibility is that there is softening of the hemicelluloses, but a percolating network does not form in modified wood. The transport mechanism presented by Jakes *et al*. showed correlation between percolation and the softening of hemicelluloses but did not prove causation. Therefore, it is possible that chemical modifications do not affect the glass transition of hemicelluloses but do prevent percolation and diffusion. In this case, even though the hemicelluloses may have softened, the heavy presence of embedded entities from the modification (e.g. acetyl groups in acetylated wood) may prevent a continuous, percolating network through which diffusion can occur.

Mechanism of decay resistance

In this case, the mechanism of decay resistance is the same as in the previous section; the diffusion of fungal CMF degradation compounds is inhibited. However, in contrast to the previous mechanism, this lack of diffusion is not related to vitrified hemicelluloses, but instead comes from lack of percolation.

Testable hypotheses of this mechanism

Similar to the previous mechanism, testing this mechanism would require testing both whether or not diffusion can occur in modified wood as well as testing whether or not the in-situ glass transition temperature of the hemicelluloses has changed. In this case, diffusion would not be observed, but the hemicelluloses would be softened.

Transport of CMF degradation agents is not inhibited

In unmodified wood, the diffusion threshold (~16% MC) (Zelinka *et al.* 2008) is well below the threshold moisture content at which brown rot decay is first observed (>20% MC) (Carll and Highley 1999, Griffin 1977, Viitanen and Paajanen 1988). Clearly diffusion is a necessary but not sufficient condition for brown rot decay to occur. Furthermore, it is unclear what other changes are occurring to the wood between the percolation threshold and the decay threshold that makes decay possible.

Previous research on modified wood has found linkages between the moisture exclusion efficiency (MEE) and decay resistance across various wood modifications (Thybring 2013) with completely different chemistry and mode of action (bulking, grafting, cross-linking). MEE is a measure at how effectively wood modifications reduce the equilibrium moisture content below fibre saturation. The relationship between MEE and decay resistance for modifications which presumably has a diverse effect on the hemicellulose softening, suggests that decay resistance may be directly controlled by the amount of water inside cell walls, although the exact mechanism is yet unclear.

One possibility is that it is not the diffusion threshold that is important to the fungi, but rather, a minimum rate of diffusion that is needed to produce a favourable decay reaction. In this case, while there may be sufficient moisture to create a percolating system, the diffusion rate is not high enough to sustain the degradation process. In terms of modified wood, it could be that even at the highest possible moisture content within cell wall diffusion is simply too slow for decay to occur (note that this does not exclude the possibility that percolation occurs in modified wood).

Conversely, it is also possible that diffusion is freely able to occur and that the decay resistance of modified wood is caused by an as yet undetermined mechanism that may or may not be related to the wood moisture content. For example, the reactions leading up to the formation of hydroxyl radicals in the CMF degradation are pH sensitive and may therefore be inhibited by the altered pH in some modified wood materials.

Mechanism of decay resistance

In this case, it is unclear the exact mechanism of decay resistance. It could be that while there is diffusion, it is not fast enough to sustain decay, or it could be that the mechanism of decay resistance is not linked to transport.

Testable hypotheses of this mechanism

If diffusion experiments show transport in decay resistant modified wood, then clearly diffusion of fungal agents is not excluded and an alternative mechanism must be responsible for the decay resistance of modified wood.

CONCLUSIONS

In this paper, we discuss newly published findings on chemical transport in wood and brown rot decay in modified woods. These new findings jointly suggest that transport of low molecular weight compounds in wood cell walls play an important role in the decay process and theories of chemical transport suggest some potential mechanisms by which transport might be inhibited. However, at this stage, there is not enough research to definitively identify the role of chemical transport in the decay resistance of modified wood. Based on the current understanding, we suggest that there are three possibilities: (1) That diffusion is inhibited by making the hemicelluloses glassy at high moisture contents (2) That diffusion is inhibited even though the hemicelluloses are softened because they do not form a percolated network, and (3) That decay resistance is not related to chemical transport. We presented several testable hypotheses to differentiate between these mechanisms with the hope that future research will be able to more clearly identify the mechanism of decay resistance in modified wood.

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Moisture Dynamics of Modified Wood and the Relevance Towards Decay Resistance

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ABSTRACT

Different initiatives related to the service life prediction of timber products and wood based panels have indicated that besides the intrinsic biological durability of the material, the wetting and drying over time is also a key parameter. Attempts to quantify this role are leading to a range of data sets according to different methodologies. Both for solid timber of different wood species and for plywood the correlation between laboratory test methods and actual time of wetness recorded in field experiments are useful and could be used as an additional approach to derive a better insight into the service life of low to medium durable materials. Considering modified wood there is a clear need to give some more consideration to the actual role and meaning of moisture content and the impact on the onset and progress of decay. This paper provides details on a range of wood modification methods (chemical wood modification, thermally modified timber, hydrophobation) in relation to water uptake and drying rate both in the laboratory and in simulated outdoor exposure approaches. Furthermore, different considerations, functionalities and hypotheses related to the importance of moisture dynamics for modified wood are presented.

INTRODUCTION

Service life prediction tools used for wood are no longer only based on the presence of active ingredients that function against biodegrading organisms. Especially when focusing on end uses related to use class 3 and to some extent also 2, the availability of water for decay fungi can be equally important. Material resistance against fungal decay of wood species and modified wood should not only be based on the intrinsic or enhanced biological durability, but should also be dealing with altered or improved moisture dynamics, meaning the ability to prevent the material getting wet to begin with (wetting ability) or staying wet (drying rate). The resulting parameter, time of wetness, is the critical parameter derived from studying moisture dynamic parameters and can be determined based on lab testing through simulation of field exposure.

In addition to the material resistance parameter ‘biological durability’ there is a need for a classification based on moisture dynamics. Prior to establishing reference materials or products for this parameter it is clear that a relevant test procedure should be available. At UGent-Woodlab work on this topic was initiated earlier with a focus on plywood. The objective was to link specific laboratory immersion tests with outdoor CMM data (Continuous Moisture Measurements) to develop the ToW concept (Van den Bulcke *et al.* 2009).

Based on this success story with plywood a similar test protocol was developed for solid wood and has since been introduced to become a CEN standard method (prEN 16818, 2015). Based on discussions to allow for testing without weekend impact and to include some longer periods for slow water uptake species it was decided to prolong the test to 144 hours and to add a submersion test with open end grain (cross cut). Meanwhile this method was part of a round robin and has been reported by Brischke *et al.* (2014).

EXPERIMENTAL

Modified solid wood

Both softwood and hardwood species were obtained partly from different research projects and compared with sets of modified wood from commercial or experimental origin. A list of wood species and modified materials used to assess moisture dynamics is presented in Table 1. This material has also been used for a more general methodological presentation by Van Acker *et al.* (2014) and the codes for the wood species is identical.

Next to radiata pine, Scots pine (heartwood and sapwood) and spruce and the modified homologues as well as European and Dahurian larch (origin Siberia) and western red cedar (WRC) were included as reference. In addition to thermally modified timber (TMT), furfurylated and acetylated radiata pine were covered. For hardwoods, low durability species, poplar and beech, were assessed in both unmodified form and thermally modified. Sapelli, European oak and teak were added as references as well as low density (obeche, limba) and higher density (ash, celtis d'Afrique) modified hardwood species.

Laboratory testing of moisture dynamics

To obtain insight into the moisture dynamics that have an impact on the time of wetness, one can consider both surface and end-grain phenomena to be relevant. The methodology developed earlier for plywood (Van den Bulcke *et al.* 2011) was based on a floating test to reveal how fast water enters through a wood surface and how easy it dries afterwards. In this concept, reference was made to testing coatings according to EN 927 part 5 and the overall methodology was proposed earlier by Rapp *et al.* (2000). As solid timber is also prone to axial water uptake, in particular when timber construction allows for some water to become trapped, a second method based on submersion was added. Both methods are briefly outlined in Table 2.

The basic idea was to start from stakes as provided for in e.g. EN 252 in ground field testing, having cross sections of 50 by 25 mm² and a growth ring angle close to 45°. The sampling procedure for the results presented in this paper focussed on having matched samples for both the floating and submersion testing. A more detailed description can be found in prEN16818 (2015) and the related IRG paper by Van Acker *et al.* (2014).

Table 1: Wood species and modified wood

Code	Full wood species name	Key botanical species	Modification
RAD PINE	radiata pine	*Pinus radiata* D.Don	-
PINE-SAP	Scots pine (sapwood)	*Pinus sylvestris* L.	-
PINE-HW	Scots pine (heartwood)	*Pinus sylvestris* L.	-
SPRUCE	Norway spruce	*Picea abies* (L.) H.Karst.	-
LARCH	European larch	*Larix decidua* Mill.	-
SIB LARCH 2	Dahurian larch	*Larix gmelinii* (Rupr.) Kuzen.	-
W RED CEDAR	western red cedar	*Thuja plicata* Donn ex D.Don	-
TM-RAD PINE	radiata pine	*Pinus radiata* D.Don	Thermal
TM-RAD PINE 2	radiata pine	*Pinus radiata* D.Don	Thermal
FU-RAD PINE	radiata pine	*Pinus radiata* D.Don	Furfurylation
AC-RAD PINE	radiata pine	*Pinus radiata* D.Don	Acetylation
TM-PINE	Scots pine	*Pinus sylvestris* L.	Thermal
TM-SPRUCE	Norway spruce	*Picea abies* (L.) H.Karst.	Thermal
TM-SPRUCE 3	Norway spruce	*Picea abies* (L.) H.Karst.	Thermal
TM-SPRUCE 4	Norway spruce	*Picea abies* (L.) H.Karst.	Thermal

Code	Wood species	Key botanical species	Modification
POPLAR	poplar	*Populus × canadensis* Moench cv 'Ghoy'	-
BEECH	European beech	*Fagus sylvatica* L.	-
SAPELLI	sapelli	*Entandrophragma cylindricum* (Sprague) Sprague	-
OAK	European oak	*Quercus robur* L. & *Quercus petraea* (Matt.) Liebl.	-
TEAK	teak	*Tectona grandis* L.f.	-
TM-POPLAR	poplar	*Populus × canadensis* Moench	Thermal
TM-BEECH 2	European beech	*Fagus sylvatica* L.	Thermal
TM-OBECHE	obeche	*Triplochiton scleroxylon* K.Schum.	Thermal
TM-LIMBA	limba	*Terminalia superba* Engl. & Diels	Thermal
TM-ASH	European ash	*Fraxinus excelsior* L.	Thermal
TM-CELTIS	celtis d'Afrique	*Celtis adolfi-friderici* Engl. & *Celtis tessmannii* Rendle	Thermal

Table 2: Floating and submersion tests to assess moisture dynamics

Parameter	Floating test	Submersion test
specimen cross section	50 by 25 mm²	
specimen length	50 mm	150 mm
edge sealing	yes	no
water penetration	one surface	whole specimens
absorption phase	1, 4, 8, 24, 48, 72, and 144 h	
desorption phase	1, 4, 8, 24, 48, 72, and 144 h	
preferred unit	g/m²	kg/m³

Field testing of moisture dynamics

The continuous moisture measurement (CMM) set up was first installed to assess the moisture dynamics of plywood (Van den Bulcke *et al.* 2009). This methodology has now been used to follow the same set of materials as detailed in Table 1. Specimens are identical to ones used for the submersion test and the edges were sealed. After installation in spring 2015, a specific rain event at the end of June was selected to analyse major differences.

Equilibrium moisture content

Wood modification in particular is considered to have a major impact on the equilibrium moisture content (EMC) of wood. The Nordic Wood Protection Council has recently added part 4 to the documents related to wood protection and used this concept to define the performance of modified wood (NWPC 2015). In a similar manner to calculating the anti-swelling efficiency (ASE) for modified wood, the moisture exclusion efficiency (MEE) is calculated as given below (Eqn. 1).

$$\mathrm{MEE} = (\mathrm{EMC}_{\mathrm{unmod}} - \mathrm{EMC}_{\mathrm{mod}})/\mathrm{EMC}_{\mathrm{unmod}} \times 100\ \% \qquad (1)$$

The approach used here sets an MEE value of 40 % to be a minimum criterion for most end uses.

RESULTS AND DISCUSSION

Laboratory testing of moisture dynamics

Van Acker and co-authors (2014) calculated mean values of 144 h absorption and desorption and ranked them both for the floating and submersion test leading to 4 rankings. Each was subdivided into 8 groupings or classes as detailed in Table 3.

Table 3: Classification of absorption and desorption for both floating (g/m²) and submersion (kg/m³) based on upper limit criteria.

Class	Floating test [g/m²]		Submersion test [kg/m³]	
	Absorption	**Desorption**	**Absorption**	**Desorption**
1	750	250	90	15
2	950	400	110	20
3	1150	500	130	25
4	1350	600	150	30
5	1750	750	170	40
6	2750	1000	210	55
7	5000	2000	250	70
8	∞	∞	∞	∞

The absorption curves fitted for both the floating test and the submersion test are based on the formula (Eqn. 2):

$$f(x) = ax^{b} \tag{2}$$

When the b-value is close to 0.5 one can expect the a value to be a parameter related to the absorption coefficient. This is based on a linear relationship with the square root of time. Deviating values of b can point at special absorption phenomena like the impact of capillary uptake. The a parameter is very good to assess the steepness of the linear area up to 4 or even 24 hours.

The desorption curves are anyhow somewhat more complex and were based on the formula (Eqn. 3):

$$f(x) = a + be^{\left(-x/c\right)} \tag{3}$$

For some species desorption resulted in a negative a value as insufficient long term desorption values were included and hence this value was set to 0 for these materials.
Van Acker *et al*. (2015) showed the potential to discriminate between species. Interpretation of the parameters here is also related to the 144 hour absorption values. The a value is the asymptotic value after drying and b the amount that is released. Hence the sum of the parameters a and b corresponds with this initial value. The parameter c corresponds with how fast the material dries, low c-values correspond with fast drying. So in summary a+b should be similar to the total absorption after 144 hours, a itself corresponds to the desorption value after 144 hours and c is an indicator for drying. High values of these 3 parameters correspond to high risk of accumulating water and hence an important time of wetness (ToW).
Results on all these parameters are given in Table 4a (softwoods) and Table 4b (hardwoods). Focussing on softwoods first and on pine in particular one can observe the highest uptake combined with a moderate drying rate in Scots pine sapwood. Radiata pine even has a lower absorption amount (but higher rate, parameter a) combined with a faster drying (desorption parameter c). European and Siberian larch are actually rather similar in behaviour when submersion is considered (open end-grain, cross section uptake). Spruce and Scots pine heartwood show a similar, rather low uptake, to Siberian larch but are slower in drying after submersion. Western red cedar is not only the lowest in absorption it also dries rather fast. All these observations mainly have an impact when wood is exposed to end grain water trapping. Focussing now on the floating test results the very fast drying of radiata pine and modified radiata pine becomes obvious, which is inevitably related to drying after a rain event on an exposed surface. This somewhat special character of radiata pine is also visible from the absorption b parameter being different from the general 0.5 value. Overall high water uptake is balanced by fast drying. This is also valid for all the modified radiata pine material although both amount and parameters can be used to differentiate. Additionally the residual moisture content also needs to be considered. The set of modified Scots pine and spruce all show a very low uptake (absorption), but also rather low drying rate (c-values).

Table 4a: Moisture dynamics parameters of softwood and modified softwood using classes as defined in Table 3 for floating (g/m²) and submersion (kg/m³)

Softwoods	Floating - absorption			Floating - desorption					Submersion - absorption				Submersion - desorption				
	Class	g/m²	f(x)=a*x^b		Class	g/m²	f(x)=a+b*exp(-x/c)			Class	kg/m³	f(x)=a*x^b		Class	kg/m³	f(x)=a+b*exp(-x/c)		
		144h	a	b		144h	a	b	c		144h	a	b		144h	a	b	c
RAD PINE	8	6729	2152	0.22	8	2741	-	6721	174	6	209	79	0.19	6	44	-	210	93
PINE-SAP	7	4256	516	0.42	7	1423	1214	3051	49	7	235	49	0.31	6	45	31	205	47
PINE-HW	4	1259	71	0.58	4	559	592	648	14	5	170	19	0.44	5	32	30	137	37
SPRUCE	5	1503	98	0.55	5	743	786	678	17	5	165	20	0.42	5	36	32	131	38
LARCH	5	1673	112	0.54	5	650	648	935	50	6	185	11	0.57	6	41	-	187	102
SIB LARCH 2	5	1505	93	0.56	5	629	631	783	48	5	169	10	0.57	6	42	11	156	90
W RED CEDAR	4	1314	85	0.55	3	401	387	881	43	4	138	20	0.39	1	12	2	135	54
TM-RAD PINE	8	5715	816	0.41	8	3705	1896	3688	206	7	248	35	0.40	8	72	36	212	84
TM-RAD PINE 2	8	6938	1666	0.30	8	4144	-	6883	300	8	383	78	0.32	8	117	20	364	109
FU-RAD PINE	7	2918	680	0.29	7	1246	-	2844	177	8	258	61	0.29	8	90	-	259	149
AC-RAD PINE	7	3355	713	0.32	7	1923	800	2463	188	6	184	27	0.39	8	69	59	124	61
TM-PINE	1	245	13	0.58	1	99	111	130	4	1	51	2	0.64	1	10	11	40	17
TM-SPRUCE	1	612	30	0.61	1	219	220	390	8	3	111	7	0.55	2	19	20	88	30
TM-SPRUCE 3	1	319	17	0.58	1	112	129	181	3	2	102	11	0.45	2	19	19	81	39
TM-SPRUCE 4	1	600	29	0.61	1	243	265	319	9	1	89	7	0.51	2	17	17	70	36

Table 4b: Moisture dynamics parameters of hardwoods and modified hardwoods using classes as defined in Table 3 for floating (g/m²) and submersion (kg/m³)

Hardwoods	Floating - absorption				Floating - desorption					Submersion - absorption				Submersion - desorption				
	Class	g/m²	f(x)=a*x^b		Class	g/m²	f(x)=a+b*exp(-x/c)			Class	kg/m³	f(x)=a*x^b		Class	kg/m³	f(x)=a+b*exp(-x/c)		
		144h	a	b		144h	a	b	c		144h	a	b		144h	a	b	c
POPLAR	6	2210	135	0.56	4	534	523	1677	29	8	264	21	0.51	6	55	30	232	63
BEECH	6	2588	143	0.58	7	1090	1112	1460	27	8	324	39	0.43	8	107	68	257	75
SAPELLI	4	1331	64	0.61	5	735	779	532	9	4	136	9	0.55	5	40	42	93	24
OAK	5	1459	105	0.53	5	687	707	730	19	5	167	15	0.48	5	40	38	127	37
TEAK	1	653	40	0.56	2	263	315	307	9	2	98	5	0.59	3	24	21	77	45
TM-POPLAR	1	557	16	0.72	1	110	135	382	10	3	111	27	0.24	1	14	12	99	36
TM-BEECH 2	3	992	51	0.59	2	348	374	568	21	5	160	14	0.50	5	37	32	128	44
TM-OBECHE	5	1392	50	0.67	2	294	104	1244	75	4	133	4	0.70	1	14	-	133	61
TM-LIMBA	2	768	31	0.64	2	291	305	440	13	5	155			5	31	25	129	50
TM-ASH	3	1099	71	0.55	2	303	328	695	35	4	134	13	0.47	4	27	27	106	39
TM-CELTIS	3	960	45	0.61	3	427	443	484	16	4	132	6	0.63	5	33	29	100	51

Differentiation is here higher when considering the submersion test. Quite a number of the modified materials show higher classification on desorption than on absorption, also in the case of radiata pine. Ease of drying after getting wet might be a more important parameter than just the ability of getting wet.

In Table 4b the same parameters are provided for hardwoods. Even more than the softwood western red cedar, teak can be considered to be an eminent wood species related to moisture dynamics, with limited absorption and a higher class for drying than for wetting. Comparing the data and the parameters of the modified hardwoods with the TMT spruce and Scots pine (Table 4a) only the thermally modified poplar shows good moisture dynamics. The values are similar to the ones determined for teak. Sapelli is equal to teak a species where the desorption class is higher than the absorption class, pointing to a low risk for moisture accumulation. Only the modified celtis allows for a similar observation, though only for the submersion test.

Field testing of moisture dynamics

Taking into account the conditioned weight of the specimens and the calculation of the starting moisture content based on the moisture control references, as well as taking into account the impact of the edge sealant on the mass recordings, the specimens' changing moisture content was recorded just before and after a rain event at the end of June 2015 alongside the actual precipitation. Moderate rainfall is considered to be between 2.5 and 7.6 mm/h. Details for softwoods are presented in Figures 1 and 2 and for hardwoods in Figure 3.

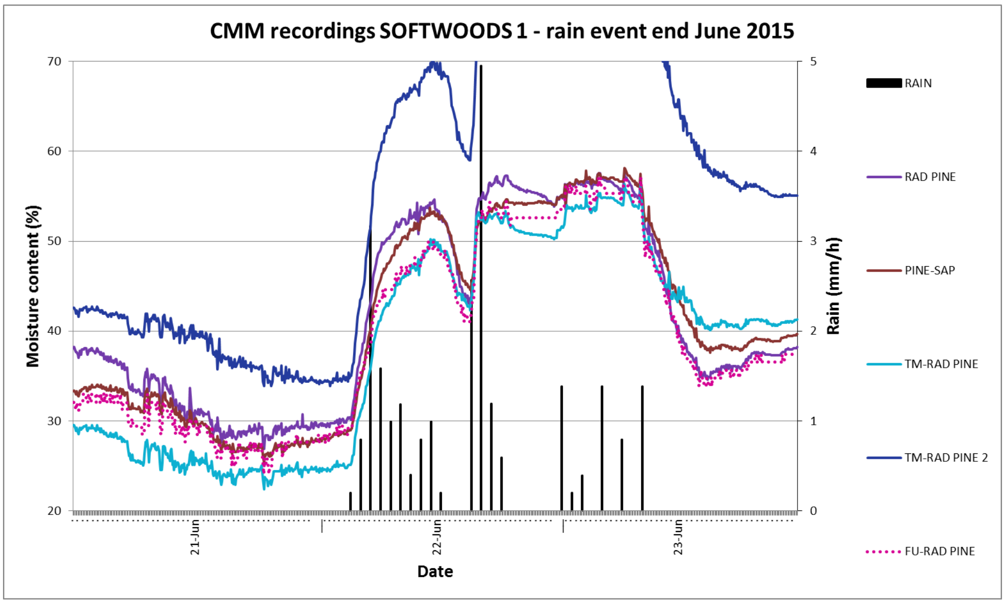

Figure 1: Field test moisture recordings (CMM) of softwoods with high absorption

The wood species with a higher water absorption showing moisture contents of over 20 % are presented in Figure 1: radiata pine, thermally modified and furfurylated radiata pine and Scots pine sapwood.

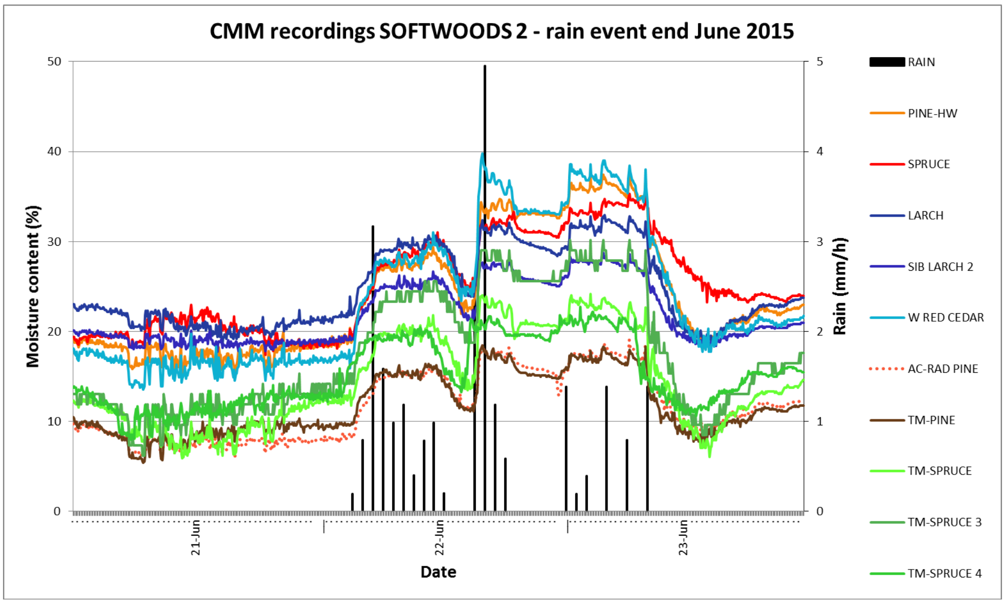

Figure 2: Field test moisture recordings (CMM) of softwoods

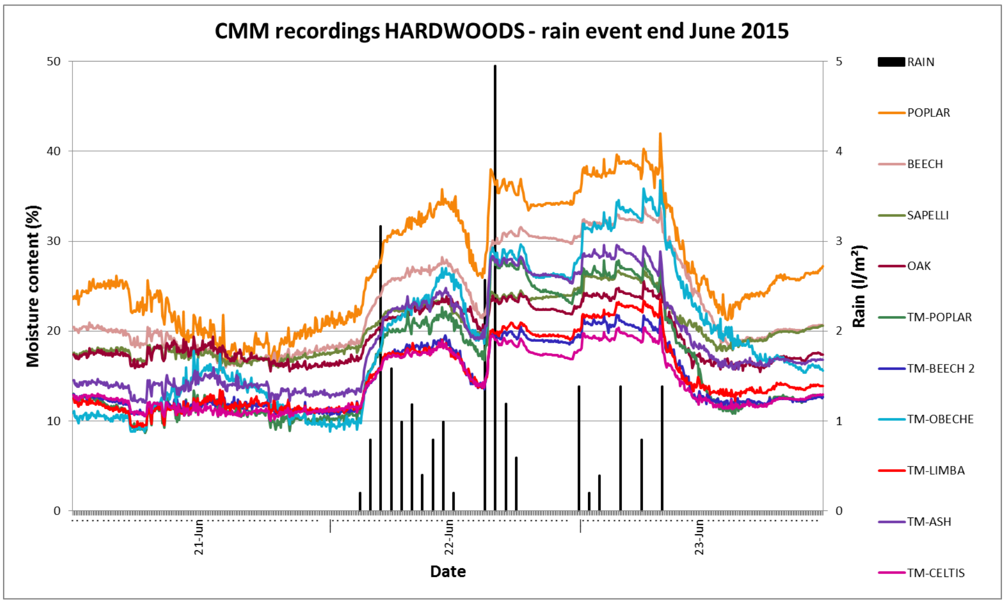

Figure 3: Field test moisture recordings (CMM) of hardwoods

The remaining softwoods presented in Figure 2 can be grouped as ones with low moisture content levels: TM Scots pine and acetylated radiata pine; somewhat higher dynamics: TM spruce; and finally the wood species western red cedar, larch species, Scots pine heart wood and spruce are the last group.

The hardwoods, as shown in Figure 3, in general overlap with the above groupings identified for softwoods. Unmodified poplar shows a similar moisture content level as spruce unmodified. Next is beech, while sapelli has an equally low moisture content during the dry periods with clearly lower absorption during actual rain. Oak shows an equally positive pattern as sapelli. TM obeche is more impacted by wetting and drying than TM ash. TM poplar, TM limba, TM beech and TM celtis in this order show lower absorption, but all arrive at a similarly low moisture content after this rain event.

Although a detailed comparison with the parameters obtained with the laboratory testing of moisture dynamics (Tables 4a & b) is possible, in general it can be observed that high absorption rate and amount of water uptake as well as the drying rate lead to a material being at risk from moisture accumulation or not, and hence showing a lower or higher time of wetness.

Equilibrium moisture content

Table 5 presents the equilibrium moisture content (EMC) values after conditioning at 65 % RH and 20 °C and the calculated moisture exclusion efficiency (MEE) values for the modified homologues.

Table 5: Equilibrium moisture content (EMC) and derived moisture exclusion efficiency (MEE) values

Species	EMC	MEE
RAD PINE	13.4	
PINE-SAP	14.6	
PINE-HW	14.1	
SPRUCE	14.9	
LARCH	13.4	
SIB LARCH 2	13.5	
W RED CEDAR	12.3	
TM-RAD PINE	9.4	29.4
TM-RAD PINE 2	9.9	26.1
FU-RAD PINE	12.2	8.4
AC-RAD PINE	3.7	72.6
TM-PINE	5.7	59.5
TM-SPRUCE	8.4	44.1
TM-SPRUCE 3	7.3	50.9
TM-SPRUCE 4	8.2	44.9
POPLAR	14.4	
BEECH	14.7	
SAPELLI	15.4	
OAK	14.5	
TEAK	11.0	
TM-POPLAR	6.8	53.1
TM-BEECH 2	8.3	43.8

Only thermally modified and furfurylated radiata pine seem to fail the criterion of 40 % MEE. However the EMC of these species is similar to, or lower than, the values recorded for western red cedar. For sure this information needs to be added to the moisture dynamic parameters as obtained by laboratory testing or field assessment. The presence of free water in the cell lumens does not necessary mean that the material is at risk of decay. A lower EMC or derived MEE is anyhow an indicator for this when discussing modified wood.

CONCLUSIONS

The material resistance to decay can be based on the presence of active ingredients that slow down or prevent degradation by specific decay organisms, but in addition it is also based on material properties that slow down wetting or limit the material staying wet. A methodology was developed to obtain as much information as possible on these moisture dynamics both focussing on face water penetration, valid for plank surfaces and most wood-based panels, and in combination with end grain penetration mainly related to water being trapping in constructions. The parameters derived are used to describe the moisture dynamics of a wood species and modified timber.

Continuous moisture measurement during a rain event allowed the confirmation of this methodology and the discussion about the behaviour of modified wood.

Furthermore, it can be concluded that the presence of water or even more so the time of wetness (time of being above a certain minimum moisture content) is not the sole factor impacting the resistance to decay. The presence of active ingredients both from natural origin or induced by wood preservation can be used to supplement or override the impact of moisture dynamics. Similarly for modified wood, the altered wetting of the cell wall and related equilibrium moisture content could be more critical than just moisture dynamics. However, this paper clearly states that both softwood and hardwood species as such, and also modified wood present a wide range of moisture dynamics and as such have an impact on the overall material durability, also considered as performance potential, or at least the resistance to decay.

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Evaluation of the Water Adsorption/Desorption Process in Chemically Modified Wood by NIR Spectroscopy

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ABSTRACT

Moisture in wood is an important factor which may affect its performance. Variation in moisture content results in dimensional and conformational instability. Attempts have therefore been made to reduce water uptake by modification of the wood material through thermal or chemical treatments. By the latter method, the hydroxyl groups in the cell wall are partially substituted. This substitution reduces the number of primary sorption sites – it is generally assumed that the hydroxyl groups are the primary sorption sites. Near infrared (NIR) spectroscopy combined with chemometric techniques is a useful tool for the structural characterisation of different materials, and also wood structure. The purpose of this study was to evaluate the interactions that appear between water molecules and the chemically modified wood structure and the mechanism of adsorption of water, by near infrared spectroscopy. Acetylated and propionylated wood samples with various weight percent gain (WPG) values and untreated reference samples were kept at three different RH levels. By increasing the WPG of the wood samples, the bands assigned to a combination of stretching and deformation vibration of the OH (1920 nm) and the first overtone of the OH stretching vibrations (1426 nm) decreased in intensity. Correlations of the data obtained by NIR spectroscopy and DVS measurements were also done.

INTRODUCTION

Wood is an important natural resource, which has many technical advantages, such as high specific stiffness and strength, low processing energy, high toughness, renewability, aesthetic properties, etc. (Popescu *et al*. 2014). However, despite these positive benefits, wood exhibits some drawbacks, such as dimensional instability in a changing moisture environment and susceptibility to fungal decay. Wood, being a hydroscopic material, when adsorbing or desorbing water vapour exhibits swelling and shrinkage in the structure accompanied by changes in its chemical, physical and mechanical properties.

Wood – water interactions have been the subject of many studies and it has been considered, first, that the water in wood may be found in three different states, i.e. free water, freezing bound water and non-freezing bound water (Nakamura *et al*. 1981). This concept was later developed and was assumed that free water is the capillary water within cell lumens, while the freezing and non-freezing bound water interacts with the wood polymers. The term ‘free’ only signifies that water molecules are not bound to specific sorption sites; it is still bound by capillary forces and has a negative water potential (Thygesen *et al*. 2010, Berthold *et al*. 1996).

The non-freezing bound water is water specifically bound to the hydrophilic sites of the three main wood components. The freezing bound water is more loosely bound water, in larger water clusters.

Chemical modification (where chemical moieties are covalently bonded to the wood cell wall polymers) is one method to improve the dimensional stability, decay resistance and water sorption characteristics of wood (Popescu *et al*. 2014). As a result, the hydroxyl groups in the cell wall are partially substituted and the cell wall of the wood is bulked with the bonded chemicals (Xie *et al*. 2011).

The substitution of the hydroxyl groups reduces the number of primary sorption sites, assumed to be the hydroxyl groups, while the bulking reduces the volume in the wood cell wall which is available to water molecules. Of the various potential chemical modification methods, acetylation, using acetic anhydride, is the most studied and acetylated wood is also produced commercially.

Papadopoulos and Hill (2003) intended to determine the mechanism by which acetylation reduces the moisture sorption of modified wood samples using a homologous series of linear chain anhydrides. In this way at comparable WPGs it was possible to have a range of levels of hydroxyl substitution. Subsequently, Hill re-evaluated this data in order to remove the effect of the weight of the bonded acyl groups (Hill 2008). The conclusion from both these studies was that the reduction in EMC was solely due to bulking of the cell wall by the covalently bonded groups and that the degree of hydroxyl substitution was not a factor.

The gravimetric method is a suitable way of determining EMC by conditioning wood samples over different saturated salt solutions to reach a certain RH, and this continues to be a popular approach even though in the last few years dynamic vapour sorption (DVS) has been increasingly used (Xie *et al*. 2011, Xie *et al*. 2010, Popescu *et al*. 2014). Even with this, the nature of the interactions between the wood components and water is not well understood. Therefore, spectral techniques such as infrared spectroscopy and near infrared spectroscopy may be able to elucidate some of these issues. Understanding sorption behaviour is important for understanding the physical and chemical changes induced by the water in wood and also the degradation mechanisms influencing the ageing of wooden structures.

As is well known, near infrared spectroscopy (NIR) offers a unique combination of speed, simplicity of sample preparation, easy use, non-destructiveness and good reproducibility, therefore it is applicable to process monitoring and quality control evaluation. Changes in the chemical composition, morphology or physico-chemical properties of materials will therefore cause spectral changes in diffusely reflected near infrared radiation. Multiple chemical absorptions considerably affect the shape of NIR spectra and lead to effects such as shifts and baseline offset (Popescu and Popescu 2013).

In the case of wood or forest products, NIR spectroscopy can be widely used in a state where not only the cellular structure, but also the bulky shape of wood is retained. Therefore it is a promising technique to analyse the physical state of such materials, as well as the chemical composition (Schwanninger *et al*. 2011) or the interaction between wood structural components and water or other chemicals (Watanabe *et al*. 2011). This technique has already been shown to be versatile in the non-destructive evaluation of the stiffness of various wood species (Meder *et al*. 2002) and structural changes during thermal treatment (Schwanninger *et al*. 2004, Popescu and Popescu 2013) or biodegradation (Ferraz *et al*. 2004). The influence of moisture content on NIR spectra has also been studied (Thygesen and Lundqvist 2000a,b, Thygesen 1994) and one or more of the water bands have been used for the determination of the water or dry matter content and it has been shown that changes in temperature also influence the band maximum position.

In the present study, the interactions that appear between water molecules and chemically modified wood structure and the mechanism of the adsorption of water has been evaluated by near infrared spectroscopy.

EXPERIMENTAL

Materials

Birch wood (*Betula pendula L*) samples of dimensions 20x20x5 mm^3 (radial x tangential x longitudinal) were used for the experiments. The samples were placed in a Soxhlet apparatus and subjected to solvent extraction for 5h using a mixture of toluene:methanol:acetone (4:1:1, by volume). The samples were air dried in a fume hood overnight and then placed in an oven set at 105 ^{o}C for 24h. After drying, the samples were removed from the oven in batches of five and transferred to a vacuum desiccator containing silica gel to cool to ambient temperature. The samples were then weighed on a four figure balance. Acetic or propionic anhydride (Aldrich, 99%+) was added to a flanged reaction flask. Then the flask was suspended in an oil bath set at 110 ^{o}C and the system allowed to reach equilibrium. Meanwhile, batches of labelled wood samples were vacuum impregnated at ambient temperature with acetic anhydride in a vacuum desiccator attached to a diaphragm pump. Acetic anhydride impregnated samples were then added to the reaction flask and at the end of the reaction period, the flask was placed in an ice bath to cool down. The samples were then removed from the acetic anhydride and acetone was added to quench the reaction. After that, the samples were extracted with a mixture of toluene:methanol:acetone (4:1:1, by volume) for 5h. At the end of the extraction period, the samples were removed and allowed to air dry in a fume hood overnight. Subsequently, the samples were transferred to an oven set at 105 ^{o}C for 24h and then weighed as before to determine the weight gain due to acetylation.

The same procedure was followed for the propionylated samples, by switching the acetic anhydride with propionic anhydride.

The weight percent gain (WPG) of the wood samples due to acetylation and propionylation was determined according to the following equation:

$$WPG\% = \frac{W_f - W_0}{W_0} \times 100 \tag{1}$$

where: W_0 is the oven dry weight of the sample before modification and W_f is the oven dry weight of the sample after modification.

In Table 1 the different values of the WPG for the acetylated and propionylated birch wood samples are presented.

Table 1: Reference and acetylated birch wood sample

Samples	WPG %
Reference	0
Acetylated	4.0
	8.8
	13.1
Propionylated	3.1
	10.4

Methods

Water uptake

The wood blocks tested were kept for 24h in an oven at 105°C to measure the dried material. In the second step the same samples were exposed, over three different saturated salts solutions, to 22, 54 and 75% relative humidity at 24°C, for a period of 48h. The weight of the samples was measured just before the spectra were recorded and no further processing of the samples was done. In Figure 1 the correlation between the adsorption curves obtained through the DVS experiments and the water uptake over three different saturated salts solutions is presented.

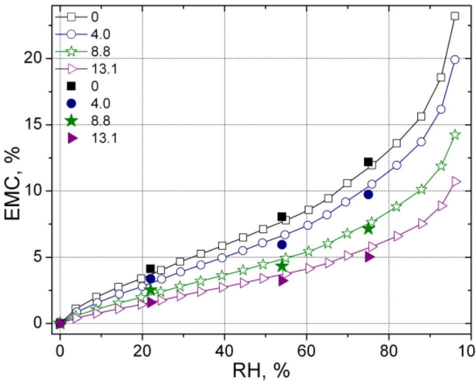

Figure 1: Adsorption curves obtained through DVS experiments (open symbols) and the water uptake over three different saturated salts solutions (full symbols)

Near infrared spectroscopy

NIR spectra were recorded using a Frontier FT-NIR Perkin Elmer spectrometer in the spectral range 1000 - 2400 nm by the diffuse reflectance method. Processing of the spectra was performed using the Grams 9.1 program (Thermo Fisher Scientific).

RESULTS AND DISCUSSION

Independently to the treatment applied, the NIR spectra show similar shapes. Figure 2 shows an example of the NIR spectrum of a dried reference birch wood sample.

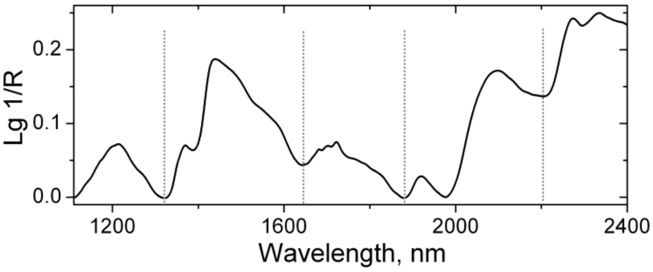

Figure 2: NIR spectrum 1110 - 2400 nm region for the extracted birch wood sample

Typical broad vibration bands associated with the chemical components of wood were identified. The spectra were separated into five spectral regions (see Figure 2):
→ 1100 – 1330 nm region – is assigned to first and second overtones of C-H stretching vibrations in methyl and methylene groups from carbohydrates and lignin (Schwanninger *et al*. 2011);
→ 1330– 1640 nm region – is assigned to first overtone of the C-H combination bands, first overtone of different O-H stretching vibrations (Schwanninger *et al*. 2011);
→ 1640 – 1850 nm region – is dominated by the first overtone of the aliphatic and aromatic C-H stretching vibrations and O-H combination bands in all wood components (Popescu and Popescu 2013, Schwanninger *et al*. 2011);
→ 1850 – 2210 nm region – is assigned mostly to C=O groups, O-H stretching and deformation vibrations, and also to C_{ar}-H and C-H stretching vibrations (Popescu and Popescu 2013, Schwanninger *et al*. 2011), and
→ 2210 – 2510 nm region – is assigned mostly to C-H stretching and C-H deformation vibrations (Popescu and Popescu 2013, Schwanninger *et al*. 2011).

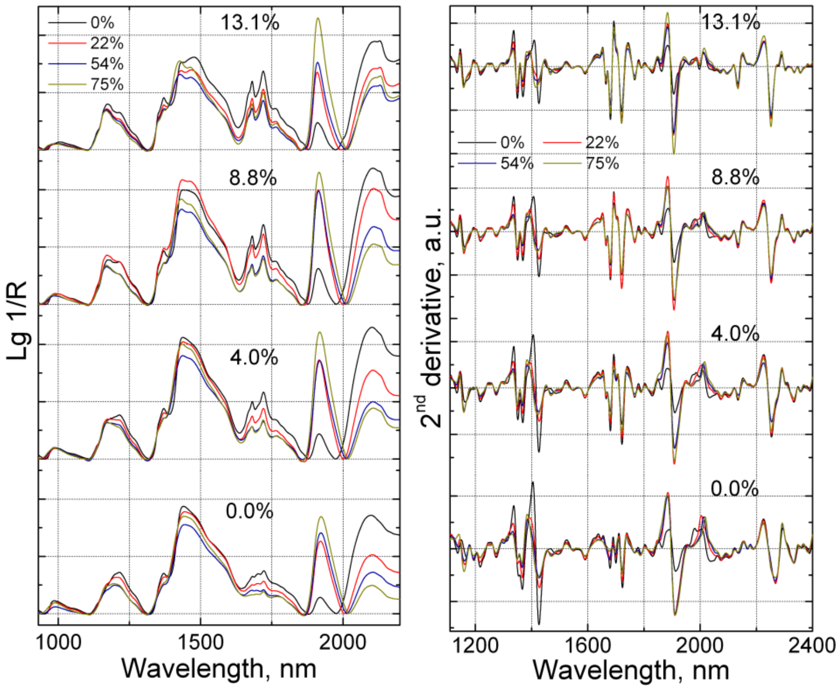

Figure 3: NIR spectra (a) and their second derivative (b) in the 930-2200 nm region for the acetylated birch wood samples exposed to different RH levels

The NIR spectra and their derivatives of birch wood samples dried and at different moisture contents are presented in Figure 3. The NIR spectra of the propionylated birch wood samples exhibit the same tendency (not shown here). As can be seen the most sensitive band to water adsorption is located at 1920 nm. This is assigned to the combination of OH stretching and deformation vibrations and increases as the RH increases.

It is well known that the integral area of a certain band is directly proportional to the amount of the species which vibrate at that certain wavelength, therefore, for a better evaluation of water uptake, subtraction of the NIR absorbance at a moisture-rich level from that of the oven-dried state was performed. After that, the values obtained were plotted against the equilibrium moisture content values from the DVS experiments (Figure 4), indicating a linear dependence.

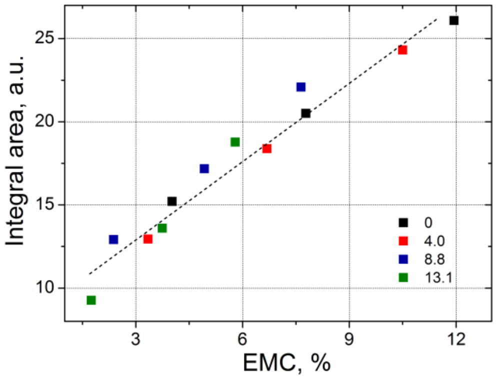

Figure 4: The integral area of the band at 1920 nm from the NIR spectra versus the equilibrium moisture content determined by DVS technique

According to literature data and from the second derivative spectra, the band at 1920 nm is a combination of three component bands located at 1907, 1962, 1997 nm.

These bands have been associated with the existence of three species of water molecules with hydrogen bond energies distributed around three maxima. Therefore, in their study Tsuchikawa and Tsutsumi (1998) assigned these bands (in Sitka spruce) to: free water molecules (S0), molecules with one OH engaged in hydrogen bonding (S1) and molecules with two OH engaged in hydrogen bonding (S2). In a more recent study of Hinoki cypress samples, Inagaki and co-workers (Inagaki *et al*. 2008) investigated different stages of these processes and observed that the water band maximum shifts to higher wavelength with increasing wood moisture content. The same behaviour was observed in the case of the birch wood samples studied in this paper.

After deconvolution of the spectra in the 1820-2030 nm region, an increase of the bands assigned to S1 and S2 components was observed, while the S0 component exhibited a certain increase in the first RH range, then a small reduction. At the same time the position of the maxima varies to lower and higher wavelengths indicating the formation of hydrogen bonding.

CONCLUSIONS

The interactions that appear between water molecules and chemically modified wood structure and the mechanism of adsorption of water were evaluated by near infrared spectroscopy.

Acetylated and propionylated birch wood samples, having different WPGs, as well as an untreated reference sample were kept at three different RH values and the water uptake was recorded and showed good correlation with DVS experiments.

From the NIR spectra and their derivatives it was observed that by increasing the WPG values of the wood samples, the bands assigned to a combination of stretching and deformation vibration for OH (1920 nm) and first overtone of the OH stretching vibrations (1426 nm) decreased in intensity, indicating a reduction in the water uptake following chemical modification.

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SESSION THREE

Poster Session 1

Birch Plywood from Thermo-Hydro Treated (THT) Veneers: Gluing and Properties

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Keywords: birch veneers, gluing, plywood, thermo-hydro treatment

ABSTRACT

In this study, thermo-hydro treatment (THT) of birch (*Betula pendula)* wood veneers was carried out. After THT, the veneers were glued using different commercial adhesives. To ensure adequate gluing quality and to improve the service properties, including biological durability, the most appropriate adhesives for THT veneers were sought. The gluing quality, according to EN 636 Class 3, was obtained with several adhesives, but their use is not economically viable for the industrial production of plywood. PF film was selected for further tests as the most appropriate adhesive for gluing THT birch veneers with respect to gluing quality and adhesive costs. Plywood samples prepared using PF film were exposed to outdoor conditions according to EN 927, and their bonding quality (EN 314) and bending strength (EN 310) were measured during a test period of 30 months. The biological durability of THT plywood was investigated after attack by the brown rot fungi *Coniophora puteana* and *Poria placenta,* and the white rot fungus *Trametes versicolor* according to the EN 12038 and EN84 tests. After 30 months outdoor exposure (EN 927), no essential changes in shear strength were observed; however, a loss in bending strength was observed. All plywood samples, including the untreated ones, are durable according to EN 12038, but after leaching according to EN 84, untreated plywood has very low durability.

INTRODUCTION

The demand for wood materials with a relatively low energy capacity for the production of products, and with competitive properties, is growing in the civil engineering and living environment, and represents one of the bases of the bioeconomy. Plywood is a high-value wood material with a wide range of applications, but to compete with low-priced products, the quality, assortment diversity and the durability are important aspects. The use of deciduous plywood in high humidity conditions is restricted by low biological durability, dimensional instability and loss in strength under the action of moisture. To ensure the designed service life in a humid environment, the durability of plywood is ensured by special coatings or impregnation. The thermal treatment of wood is an alternative to chemical protection with biocides. It is comparatively widely used to improve the durability of solid wood. Thermally treated plywood has been investigated much less. There are studies on plywood from thermally treated hornbeam (Schulz *et al.* 2012) and poplar (Zdravković *et al.* 2013) veneers. However, commercial production has not yet developed, although, even in 2006, its development within the next 2-5 years was forecast (Jones and Enjily 2006). One of the problems is the inadequate gluing quality after gluing thermally treated veneers with industrial plywood glues (Blüthgen and Schulz 2008). The biological durability of PF resins, which are traditionally used in plywood manufacturing, is also questionable and there are indications that they are biodegraded by white rot fungi (Gusse *et al.* 2006).

EXPERIMENTAL

The THT of 70 birch (*Betula pendula*) veneer sheets was carried out in a WTT multi-functional pilot scale modification device in elevated water vapour pressure conditions under two different treatment regimes: 160/3 and 170/1 (temperature,˚C/duration, h). Plywood samples with dimensions of 850 x 350 mm were glued with different adhesives from 9 layers of THT veneers. 6 parallel samples were used. Exposure to outdoor conditions was carried out according to EN 927. Bonding quality was determined according to EN 314 after treatment of the plywood samples in water at room temperature and in boiling water. Bending strength was determined according to EN 310 and biological durability according to EN 12038 and EN 84.

RESULTS AND DISCUSSION

To ensure the gluing quality and to improve the service properties, including biological durability, the most appropriate adhesives for THT veneers were sought. Using melamine-urea-formaldehyde (MUF) binders, similar results to those of the PF adhesive were obtained, but the lowest gluing strength was for the samples glued with polyurethane (PU) glue. The gluing quality, in compliance with the Standard EN 636 Class 3, was obtained with the urethane type glue, water dispersion glue and special PVA glue; however their use is not economically viable for the industrial production of plywood. Surprisingly, high values were demonstrated by the plywood, made from THT veneers glued with PF film. The costs of the PF film per 1 m^2 are 10-fold higher than traditionally used PF resin adhesive, but half that of urethane glue. The use of the PF film for gluing THT birch veneers is a good alternative for plywood production, which is feasible and has comparatively low costs; therefore, for further tests, THT veneers were glued with the PF film and tested.

For the untreated and THT plywood samples, tested after 30 months exposure outdoors (EN 927-3), no essential changes in shear strength were observed in either bonding quality determination methods according to EN 314 (Table 1).

Table 1: Bonding quality (EN 314) of plywood made from THT veneers using the PF film as an adhesive during outdoor exposure (EN 927)

Treatment temperature (°C)/ time (h)	**Bonding quality determination according to EN 314**	**Testing time according to EN 927 in months**					
		0	**6**	**12**	**18**	**24**	**30**
		Shear strength (N/mm^2)					
Untreated	In boiling water	1.7	2.1	1.8	1.4	2.1	1.7
170/1		1.0	0.9	0.9	0.9	1.1	1.0
Untreated	In water at room temperature	3.1	2.9	3.3	2.7	2.6	2.8
160/3		2.7	3.1	2.2	2.0	2.5	2.6
170/1		2.3	1.9	2.5	2.0	1.9	2.0

The bonding quality for untreated plywood in both test procedures was higher than that of THT plywood; however, bonding quality Class 3 according to EN 636 after 30 months of exposure outdoors was maintained.

The bending strength of untreated samples and plywood made from THT veneers had a tendency to decrease during 30 months of exposure outdoors (Table 2) in both the grain directions tested. It is difficult to assess these changes because the number of samples tested after each period (6 months) was very small (only 3) but, in general, the loss of bending strength after 30 months of outdoor exposure was 17-42% for untreated samples, 16-21% for THT samples at 160°C/3h and 23-38% for THT samples at 170°C/1 h.

Table 2: Bending strength (EN 310) of plywood made from THT veneers using the PF film as an adhesive during outdoor exposure (EN927)

Treatment temperature (°C)/time (h)	**Testing time according to EN 927 in months**					
	0	**6**	**12**	**18**	**24**	**30**
	Max force in N parallel to the grain					
Untreated	1818	1419	1567	1536	1039	1046
160/3	1286	1346	1236	1321	1051	1015
170/1	1364	1139	1170	1196	975	1052
	Max force in N perpendicular to the grain					
Untreated	1437	1199	1144	1208	1298	1183
160/3	1703	1506	1501	1616	1513	1431
170/1	1607	1465	1197	1100	1286	995

An essential aspect is the better biological durability of THT plywood. Mass losses (ML) in the tests (EN 12038) after the action of *C. puteana, P. placenta* and *T. versicolor* were in the range from 0.1 to 1.4% and did not differ considerably from those for untreated plywood (Table 3). In this case, all types of plywood were very durable according to EN 350-1. Our results agree with the data of other authors (Dieste et al. 2008, Curling and Murphy 1999). However, essential distinctions were observed after leaching of the samples according to EN 84: the ML of untreated plywood exceeded 20%, which is completely unacceptable for a bio-durable material, and also the ML of THT plywood reached 5% in the case of *P. placenta* and *T. versicolor.* There is no consensus yet on the reasons for the reduced biodurability of plywood after leaching; though volatile compounds could inhibit the action of fungal development in closed test vessels.

Table 3: Decay resistance – ML of THT veneers after attack by the brown rot fungi C. puteana and P. placenta, and the white rot fungus T. versicolor according to the tests EN 12038 and EN84

Treatment temperature (°C)/time (min)	**EN 12038**			**EN 84 and EN 12038**		
	C. puteana	***P. placenta***	***T. versicolor***	***C. puteana***	***P. placenta***	***T. versicolor***
Untreated	0.3	0.0	0.5	29.8	20.7	29.8
160/3	1.1	0.1	1.4	2.6	5.0	5.3
170/1	0.2	0.0	1.0	0.0	1.3	3.5

Our results on the biological durability of THT plywood after a prolonged evaporative ageing procedure (EN 73), together with data on veneer and plywood chemical component composition and the chemical analysis of water extractives (after EN 84), will give additional information for understanding the biological durability of plywoods.

CONCLUSIONS

Suitable gluing quality was obtained with several adhesives tested, but their use is not economically viable for the industrial production of plywood. Using a PF film as an adhesive for gluing THT birch veneers, a material with a bonding quality appropriate for Class 3 (plywood applicable in outdoor conditions) according to EN 636, was obtained. Bonding quality was higher in untreated plywood than in the THT samples. Changes in the bonding quality of the plywood obtained were not constitutive during 30 months of exposure outdoors according to EN 927.

The bending strength of untreated plywood and plywood made from THT veneers decreased during 30 months of exposure outdoors.

All samples, including untreated plywood, are biologically durable according to EN 12038, but after leaching according to EN 84, untreated plywood has a very low durability and also THT plywood has a higher ML.

The results obtained testify that it is possible to produce plywood with improved service properties from THT birch veneers, choosing the appropriate adhesive and gluing technology.

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Colour Responses of Thermally Modified *Eucalyptus globulus* from Galicia to Artificial Weathering

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Keywords: *Eucalyptus globulus*, heat treatment, artificial weathering, colorimetry, surface modification, wood quality.

ABSTRACT

Eucalyptus globulus is one of the most profuse wood species in Galicia, northwest Spain, and is widely used to produce, primarily, cellulose pulp and, secondly, panels and boards. Blue-gum eucalypt is not favoured for its natural colouration, a monotonous light brown colour, and hence this species is rarely exploited as massive wood. A possible valorisation process is heat treatment, which can improve the hydrophobicity and the weathering resistance of the wood surface, important for outdoors applications, and also darkens the material so that similar aesthetic properties to highly-priced tropical woods can be obtained. In this research, many *Eucalyptus globulus* samples underwent different core and surface heat-treatments and exposed to a QUV artificial weathering process. The heat-treated and the weathered surfaces were regularly monitored for their surface chemistry with spectroscopic techniques. CIELab colorimetry measurements were made during the modification processes in order to get a quantitative description of the appearance of this timber. The colour of some heat-treated samples was darker and more attractive for aesthetic purposes, thus increasing the value of this timber in aesthetic applications. In addition, those samples, treated at the highest temperatures, also presented better colour stability during artificial weathering than the untreated ones.

INTRODUCTION

Wood as a biological material is susceptible to environmental degradation when it is used outdoors. The main agents responsible for the natural degradation and consequently physical changes of the wood surface, such as discoloration, are moisture (dew, rain and snow), solar electromagnetic radiation (UV, visible and infrared light), heat, molecular oxygen, wind and certain specialized microorganisms, which can act alone or in combination (Feist 1990).

Ultraviolet light is one of the factors that can most notably cause severe changes in the appearance of the wood surface. The photochemical degradation of an exposed wood surface from sunlight occurs in a short time and the irradiated wood may exhibit a loss of gloss, cracking, roughening of the surface and weight loss. All these changes are caused by chemical modifications of the structure of cellulose, hemicelluloses and lignin (Hon and Feist 1992). Colour changes on the wood surface are a direct indication of the chemical modification in the cell wall due to weathering, whereas the rate of discoloration is related to the intensity and duration of the UV irradiation together with the species of the wood (Ozgenc *et al.* 2012).

In thermally modified wood, the physical and chemical properties are altered by subjecting the material to high temperatures. Heat treated wood can be used outdoors for cladding and decking because of its improved dimensional stability and durability compared to unmodified wood (Militz 2008). In terms of weathering resistance, it has been reported that the short-term colour stability of thermally modified timber exposed to artificial UV radiation performed better than untreated wood (Ayadi *et al.* 2003). In addition, the treatment darkens the wood and may provide a uniform surface, which can add market value to less attractive species like *Eucalyptus globulus* whose natural colour is not very much appreciated in the markets.

This study represents the first attempt to get a new insight into the different coloration behaviour of eucalypt wood subjected to heat treatment in the range 140-220ºC. The colour differences were analysed during and after 504 hours of artificial weathering, using the equation best suited to correlate visual perceptions and quantitative measurements, CIEDE2000 (CIE 2001). The study tries to provide knowledge about the different colour behaviour of the thermally modified *Eucalyptus globulus* with the objective of increasing the market value of this wood by giving it a more attractive and stable colour.

EXPERIMENTAL

Wood material and treatment

Raw boards from the heartwood of *Eucalyptus globulus* obtained from trees older than 25 years harvested in Galicia, Spain, with diameters larger than 45 cm were used for the experiments. All the boards selected for testing were free from surface defects, such as cracks, knots, bending, etc. The samples were cut to different dimensions and were kept in a conditioned room at 23˚C and 65% relative humidity until stabilized.

Prior to heat treatment, the samples were dried in an electrical resistance oven equipped with a system for air circulation at 103ºC until reaching constant weight. This previous drying procedure was aimed at eliminating the effect of wood moisture on the thermal modification process. The heat treatments were performed in the same oven in the presence of air at 140, 160, 180, 200 and 220˚C for 6 hours.

Artificial Weathering

A series of 3 samples of dimensions 150 x 75 x 20 mm^3 (L, R, T) for each heat treatment, and also for untreated *Eucalyptus globulus*, were exposed to artificial weathering. The simulated weathering was carried out in a QUV/spray accelerated weathering tester (Q-Panel Lab Products Cleveland, USA) according to the guidelines of EN 927-6 (2006). The exposure cycle started with a condensation phase (4 hours at 40˚C), followed by UV-light (8 hours at 60˚C) with UVA-430 lamps and water spray. The artificial weathering test was performed for a period of three weeks (504 hours).

The wood colour was measured with a Mercury 2000 spectrophotometer (Datacolor). The diameter of the spotlight used for measurement was 11mm. The wood colour was determined according to the CIELAB space with CIE standard illuminant D65 and a 10˚ standard observer, with nine measurements per sample. The variation in colour as a function of irradiation time was calculated according to the CIEDE2000 (2:1:1) colour difference equation (Eqn. 1).

$$\Delta E_{00} = \sqrt{\left(\frac{\Delta L'}{k_L S_L}\right)^2 + \left(\frac{\Delta C'}{k_C S_C}\right)^2 + \left(\frac{\Delta H'}{k_H S_H}\right)^2 + R_T\left(\frac{\Delta C'}{k_C S_C}\right)\left(\frac{\Delta L'}{k_L S_L}\right)} \qquad (1)$$

RESULTS AND DISCUSSION

The colour of the thermally modified samples was uniform over the surface, and it can be observed that six hours of treatment at 140 and 160˚C did not produced significant colour changes (see the first three columns of row A in Fig. 1), whereas a noticeable colour change can be appreciated at a treatment temperature of 180˚C and beyond. At the highest temperatures, *i.e.* 200˚C and 220˚C, the aesthetic modification becomes more evident until the colour reaches a dark brown shade.

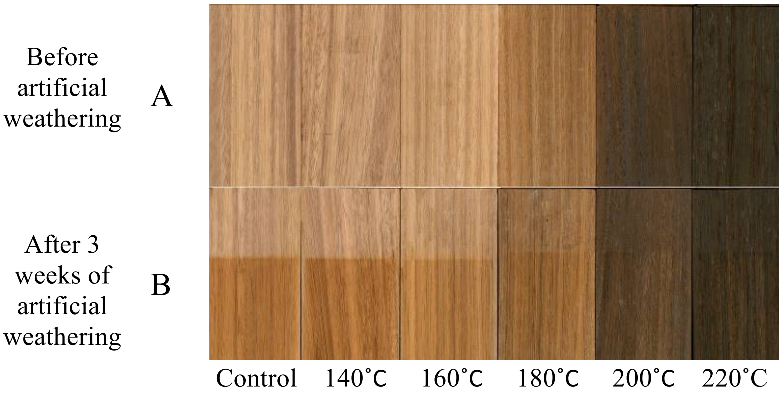

Figure 1: Effect of thermal modification only (A) and after artificial weathering (B) on colour of untreated and heat-treated samples

From a visual evaluation of row B in Fig. 1 it is possible to appreciate the colour changes caused by 504 hours of artificial weathering exposure, which are more noticeable in the lighter samples (*i.e.* control, 140 and 160˚C). In these samples, a darker region can be easily seen, which corresponds to the part exposed to weathering.

The colour change caused by artificial weathering in the untreated and treated samples at 140 and 160˚C is indicated by a decrease in the lightness values (L^*) and an increase in the cromaticity parameters a^* and b^* (see Fig. 2 A, B and C respectively). The colour stability of the material, untreated and heat-treated, has been also examined by means of the extent of colour difference ΔE_{00} (Fig. 2 D).

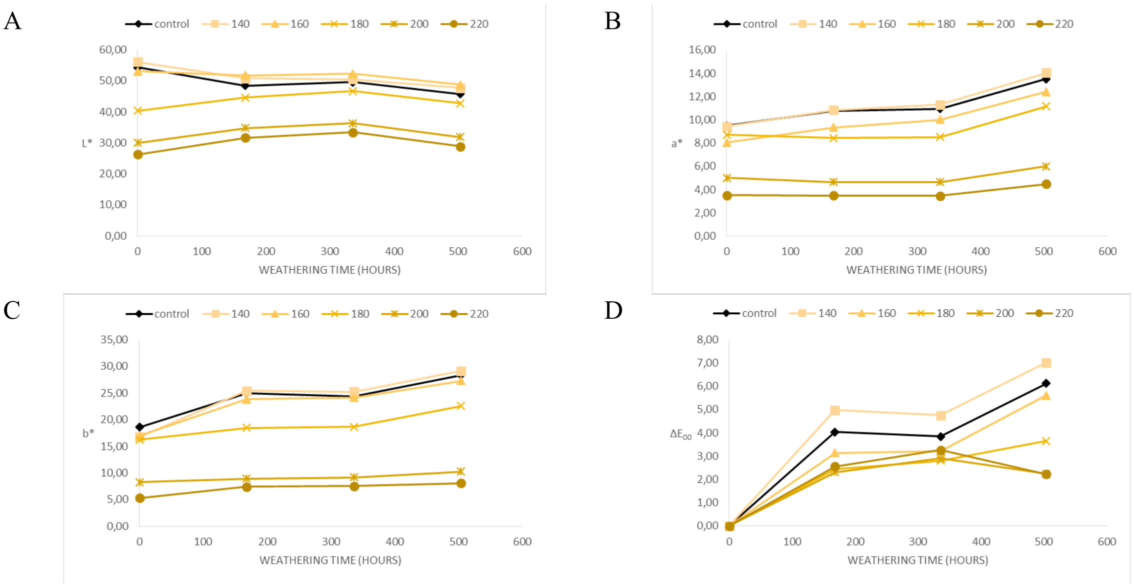

Figure 2: Effect of artificial weathering on colour parameters: (A) L*, (B) a*, (C) b* and (D) ΔE_{00}

The colour modifications caused by artificial weathering were found to be softer in the case of samples treated at 200 and 220˚C where the registered ΔE_{00} was three times lower than the untreated wood. This means that higher colour stabilty has been achieved by thermal treatment. Conversely, the samples treated at 140˚C were the group that showed the strongest variation in colour after 504 hour of exposure, exhibiting even higher variability than the control samples.

CONCLUSIONS

The dark brown colour of blue gum eucalypt thermally modified at 200 and 220˚C presented higher stability after 504 hours of artificial weathering than the other groups tested (*i.e.* untreated and samples treated at 140, 160 and 180˚C). In addition, the heat-treated wood in that temperature range also showed a uniform and attractive surface colour, which is more suitable for aesthetic applications such as furnishing, indoor decoration and wood finishing.

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Determination of Extractives Composition in Thermo-Treated Wood

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ABSTRACT

It is well known that through adequate modification processes it is possible to improve wood properties, deriving a new and environmentally friendly material. The performance of wood products may be influenced by their chemical compounds such as extractives, which contribute to the protection of wood from decay, affect the degree to which the color changes upon exposure to light and improves its dimensional stability. In addition, extractives may influence gluing, finishing, papermaking and contribute to the corrosion of metals in contact with wood. Twenty sawn boards of Deodar cedar (*Cedrus deodara* Roxb) and Italian alder (*Alnus cordata* Desf) were used to investigate the effects of a heat treatment on the extractive content of wood. The component groups in the extracts were determined by gas chromatography in combination with mass spectrometry (GC-MS). The results showed that different types of polyaromatic compounds were produced in the thermo-treated wood.

INTRODUCTION

In the last decade several research groups have developed heat treatment methods for wood suitable for industrial applications. Heat treatment has been reported to be an effective method of improving the dimensional stability and durability of wood, as well as changing low-value species into higher value materials without the use any chemical additives (Esteves and Pereira 2009). The effect of steam and heat on wood involves changes in the physical and chemical nature of the wood microstructure as well as in the cell wall components. In relation to extractives, the most volatile compounds leave the wood, whilst other ones degrade. In this sense, after degradation, new chemical compounds may be obtained, for example new extractives generated by the degradation of the polymers. Extractives can be implicated in most of the properties of wood and in the performance of wood products, because they can protect wood from decay, affect the degree to which the color changes upon exposure to light, the odor of the wood and the accent of the grain pattern. A large number of the compounds in extractives from different trees have been identified and they represent many classes of organic compounds. The qualitative and quantitative analysis of extracts of several plant materials has been undertaken (Fernandez *et al.* 2001). Sugars and fats, amino acids and carboxylic acids are primary metabolites, which are always present in the extract. With regard to secondary metabolites, some studies focus only on the analysis of a given group of extractives (Claassen *et al.* 2000). The main goal of this work focuses on the analysis, by gas chromatography-mass spectrometry (GC-MS), of extractives that are present in heat-treated and untreated Deodar cedar (*Cedrus deodara* Roxb.) and Italian alder (*Alnus cordata* Desf.). The impact of the heat treatment conditions on the chemical composition, in particular on the composition of extractives, has been studied.

EXPERIMENTAL

Wood material

Boards of alder and cedar, measuring 50 x 6 x 180 mm, were cut into small pieces to ease the grinding step. The samples were dried until their moisture content was 0%, and then thermally treated at 200 °C for 3 hours in a thermo-vacuum cylinder (WDE-Maspell s.r.l., Italy).

Determination of Extractives and Gas Chromatography-Mass spectrometry

Treated and untreated wood samples were first powdered and then extracted in a Soxhlet apparatus to determine the extractives content. The method used was TAPPI CPPA G 13 as described in Solvent Extractives in Pulp (1997); this method determines the amount of solvent-soluble, non-volatile material in wood. One gram of milled wood sample was extracted using a mixture (2:1) of benzene (99 %) and ethanol (96 %). For the extraction the Soxhelet apparatus was used with 300 ml of the 2:1 benzene/ethanol mixture for 7 h. After the extractions, the solution was dried in a previously weighed 25 ml flask using a rotary evaporator connected to a vacuum pump (Vacuumbrand PC3001). The percentage of extractives was determined by weighing the flask containing the residue and after doing the analysis of the extractives, GC-MS was carried out.

The GC-MS analyses were performed on a Hewlett Packard GC-MS, HP 6890 GC system equipped with HP 5973 Mass selective detector, using a high-temperature capillary column (HP-5MS, 30 m × 0.25 mm I.D., 0.25 µm film thickness; J&W Scientific). Helium was used as the carrier gas. The samples were injected directly into the column. The temperature during the injection was 80 °C and after the injection was programmed to remain at 80 °C for 3 min, then to rise to 250 °C at a rate of 20 °C min^{-1} and hold for 20 min. The compounds were identified by computer comparison of the mass spectra with NIST libraries and by mass fragmentography.

RESULTS AND DISCUSSIONS

The quantities of extractives that were found in the untreated wood were found to be greater than those obtained from treated wood (Table 1).

Table 1: Summary of the extraction of experiments, the amounts of extracts

Solvent	Alder extracts		Cedar extracts	
	Untreated [g]	Heat treated [g]	Untreated [g]	Heat treated [g]
Benzene/Ethanol	0.0819	0.0225	0.1082	0.0890

These data are in agreement with the increase in the cross-linking of thermally treated wood compared to untreated wood. This because during thermal treatment polycondensation reactions with other cell wall components occur, resulting in further cross-linking (Boonstra and Tjeerdsma 2006). This cross-linking makes it difficult to extract the chemical compounds probably due to incorporation of extractives in the structure of the wood.

The identification of the peaks in Alder obtained from the benzene/ethanol extraction is listed in Tables 2 and 3, while the peaks in cedar are shown in Tables 4 and 5.

Table 2: Peak assignment on the GC-MS analysis of samples of alder untreated

Retention Time (min)	Area %	Compound
10.04	0.8	Benzophenone
11.27	3.1	Isobutyl-*trans*-hex-3-enyl phthalate
11.49	6.9	1-Methyldodecylbenzene
14.84	2.6	Eicosane
16.04	2.6	Octacosane
17.58	2.6	2-Methyloctacosane
19.54	2.0	Heptacosane

Table 3: Peak assignment on the GC-MS analysis of samples of thermally treated alder

Retention Time (min)	Area%	Compound
7.81	1.1	Glycerol 1,2-diacetate
7.89	1.3	2,6-Dimethoxyphenol
8.32	2.8	Vanillin
8.47	2.2	3-Hydroxy-4-methoxybenzaldehyde
9.18	5.9	Butylated Hydroxytoluene
9.25	1.7	Butylated Hydroxytoluene
9.84	1.5	1-Methylethyl dodecanoate
10.00	0.7	Benzophenone
10.15	12.5	4-Hydroxy-3,5-dimethoxybenzaldehyde
10.60	15.6	4-Hydroxy-2-methoxycinnamaldehyde
10.77	4.8	3,5-Dimethoxy-4-hydroxyphenylacetic acid
11.28	6.4	Isobutyl-octyl phthalate
14.90	33.3	Bis(2-ethylhexyl) hexanedioate

Table 4: Peak assignment on the GC-MS analysis of samples of untreated cedar

Retention Time (min)	Area %	Compound
8.93	2.7	2,4a,5,6,7,8,9,9a-Octahydro-3,5,5-trimethyl-9-methylene- (4a*S*-*cis*)-1*H*-benzocycloheptene
9.12	2.3	*Cis* (-)-2,4a,5,6,9a-Hexahydro-3,5,5,9-tetramethyl-1*H*-benzocycloheptene
9.26	7.5	2,4a,5,6,7,8-hexahydro-3,5,5,9-tetramethyl-1*H*-benzocycloheptene
9.48	0.7	1,1,2,2,3,3-Hexamethylindane
9.73	2.6	4-(2-Benzothiazolyl)fuzaran-3-amine

Table 5: Peak assignment on the GC-MS analysis of samples of thermally treated cedar

Retention Time (min)	Area %	Compound
8.94	0.8	2,4a,5,6,7,8,9,9a-Octahydro-3,5,5-trimethyl-9-methylene- (4a*S*-*cis*)-1*H*-benzocycloheptene,
9.12	1.5	*Cis* (-)-2,4a,5,6,9a-Hexahydro-3,5,5,9-tetramethyl-1*H*-benzocycloheptene
9.26	5.6	(*R*)-2,4a,5,6,7,8-Hexahydro-3,5,5,9-tetramethyl-1*H*-benzocycloheptene,
11.28	15	Hept-4-yl-isobutyl phthalate
16.40	7.3	(2,4a,5,6,7,8-Hexahydro-3,5,5,9-tetramethyl-1*H*-[7]annulen-1-yl)methanol
17.48	15.2	(4-benzylphenyl)(p-Tolyl)mathanone
18.96	4.5	(4-benzylphenyl)(4-(hydroxymethyl)phenyl)methanone

During heat treatment the original extractives disappear or degrade (Burgois *et al.* 1989). Generally, in both treated woods more compounds were identified. This suggests that for untreated wood the extractives are molecules relatively larger than in treated wood, whereas after treatment the smaller molecules obtained can be more easily identified using GC-MS. Analysis of the extractives of treated and untreated cedar showed compounds similar to each other and belong to the class of terpenes, whereas analysis of the Alder chromatograms showed differences in the chemical compounds. In particular, for treated alder, compounds at 16.40 min, 17.48 min and 18.96 min were additionally found compared to untreated alder. For alder the extractives are for the most part esters.

CONCLUSIONS

Different types of polyaromatic compounds were produced by the thermal treatment of wood, with some difference between species probably due to their different wood structure. The quantity of extractives that was found in untreated wood was greater than that obtained from treated wood. In the case of both species the total amount of compounds that could be identify was less than in the untreated wood compared to the treated wood. Analysis of the extractives from treated and untreated cedar show compounds similar to each other which belong to the class of terpenes, whereas most of the compounds observed in the treated alder were esters.

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Surface Properties and Set Recovery of Silver Birch and European Aspen Wood after Industrial Scale Compression and Thermal Modification

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Keywords: anatomy, Brinell hardness, CIEL*a*b*, colour, density

ABSTRACT

The objective of the study was to determine the effect of compression and subsequent thermal modification on the colour, density, Brinell hardness, cell deformation and long-term dimensional stability of sawn *Betula pendula* and *Populus tremula* wood. Sawn timber was modified in an industrial sized pilot device capable of drying, compression and thermal modification. The starting phase of compression had an effect on the magnitude of densification. Densification occurred mainly in the earlywood of each annual ring near to the surface. The colour of the wood was at its darkest near to the most densified annual rings, and most often near to the surface. Compressing green sawn timber and using thermal modification after compression reduced the set recovery behaviour. Problems related to the set recovery of compressed wood can be decreased, though not eliminated, using post compression thermal modification.

INTRODUCTION

Compression is a process whereby the density of wood is increased by reducing the void volume of the lumens in order to improve selected mechanical and physical properties and dimensional stability (Navi and Girardet 2000, Navi and Sandberg 2012). The viscoelastic nature of wood plays an important role in compression. The compression of wood perpendicular to the grain requires that the cell walls are in a rubbery phase in order to obtain compression deformation without cell wall fractures (Hillis and Rozsa 1978, Kutnar *et al*. 2009). In earlier studies, the compression of wood was only combined with heat. More recent studies have applied compression to wood in the presence of heat as well as steam together with a combination of hydrothermal post-treatment to ease the process by softening the wood and to improve dimensional stability (Inoue *et al*. 1993, Navi and Girardet 2000, Laine *et al*. 2013). Gradual set-recovery facilitated by changes in the moisture content of wood is the main drawback of the compression treatment. A lot of work has been carried out since the early 20th century to develop industrial wood compression and stabilization methods (*e.g,* Rowell and Konkol 1987, Rautkari 2012). However, only a few production scale applications have been commercialised, one of them is introduced in this paper. The objective of this study was to investigate an industrial application, where drying and the thermal modification of solid wood are carried out in a compressed state in order to densify the boards in the direction of their thickness, and to enhance the product characteristics.

EXPERIMENTAL

European aspen and silver birch boards were sawn from freshly harvested logs, to a length of 2,700 mm and nominal cross-cut dimensions of 40×100 mm. The four different combinations of modification processes were carried out in a pilot modification kiln patented by Korwensuun Konetehdas Ltd, Finland, which allows drying, compressing and thermal modification in a single process (Table 1). During the process, the wood temperature was first increased gradually up to 100 ºC and stabilized until the MC of wood reached a level of 30%. Once below 30% MC, the wood temperature was raised to 130 ºC for the rest of the drying phase. The target degree of compression for birch and aspen were set to 10% and 30%, respectively. Further on, half of the material was thermally modified at 190 °C after the drying and compression phases. The reference boards were air dried until they reached a final MC of 8–10%.

Table 1: Combinations of compression and thermal modifications used in the processes

Process	N	Compression		Thermal modification
		Starting of compression	Target degree of compression	
Birch G	28	Green	10%	-
Birch G + TM	28	Green	10%	3 hours at 190°C
Birch MC20	24	At 20% MC	10%	-
Birch MC20 + TM	24	At 20% MC	10%	3 hours at 190°C
Aspen G	28	Green	30%	-
Aspen G + TM	28	Green	30%	3 hours at 190°C
Aspen MC20	28	At 20% MC	30%	-
Aspen MC20 + TM	28	At 20% MC	30%	3 hours at 190°C

G = compression started with green wood, MC20 = compression started at 20% MC,
TM = thermal modification, N = number of specimens

The density profiles of the compressed and reference specimens were measured using X-ray microdensitometer in the direction of board thickness and transformed to density values at relative depths in order to compute the mean density profile within each process. Specimens with lengths of 300 mm were prepared from each board for reflectance spectra and Brinell hardness measurements at different depths (0, 3, 6, 9 and 12 mm) from the original surface of the boards. Reflectance spectra were converted to CIEL*a*b* colour coordinates using a 2° standard observer and D65 light source and the colour difference ($\Delta E_{ab}*$) between the modified and unmodified specimens was calculated using CIE76 standard (Hunt 1998).

RESULTS AND DISCUSSION

Compression of aspen boards resulted in a maximum density at the surface or at a depth of 3–5 mm from the surface when the compression was started in the green state (Fig. 1). The difference in density between the MCs at the time of compression indicates that the compression of wood is the highest at the location of the highest MC when there is variation in MC across the board thickness (*cf.*, Rautkari *et al.* 2011). Densification occurred mainly in the earlywood of each annual ring near to the surface. The combined compression and thermal modification reduced the lightness of wood and increased its redness compared to unmodified wood, which increased ΔE* (Fig. 2). The colour differences between the surface and inner parts were greater for birch than for aspen. The highest Brinell hardness was recorded at a depth of 6 mm in aspen and at a depth of 12 mm in birch (*cf.*, Heräjärvi 2009). With aspen, it was obvious that the average Brinell hardness was greater when compression was started from the green state than when it was started at 20% MC. With birch, the lowest Brinell hardness values were recorded for the sawn timber, which was compressed starting in the green state and subsequently thermally modified. Dimensional changes due to swelling through water immersion were the greatest for compressed green specimens without thermal modification, in the case of both birch and aspen (Fig. 3). The maximum swelling of the compressed specimens was significantly decreased by the application of thermal modification. Aspen wood showed a greater tendency to dimensional changes than birch wood.

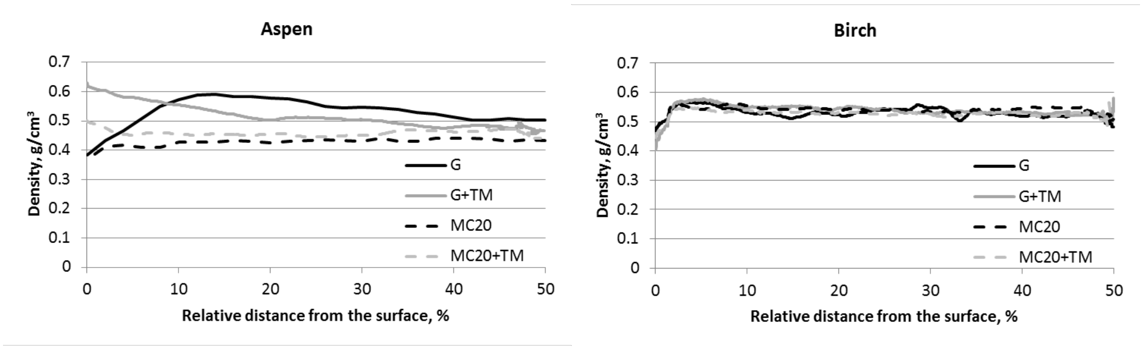

Figure 1: Mean density of wood through the thickness profile of compressed aspen and birch specimens (0 = surface of the board, 50 = centre of the board)

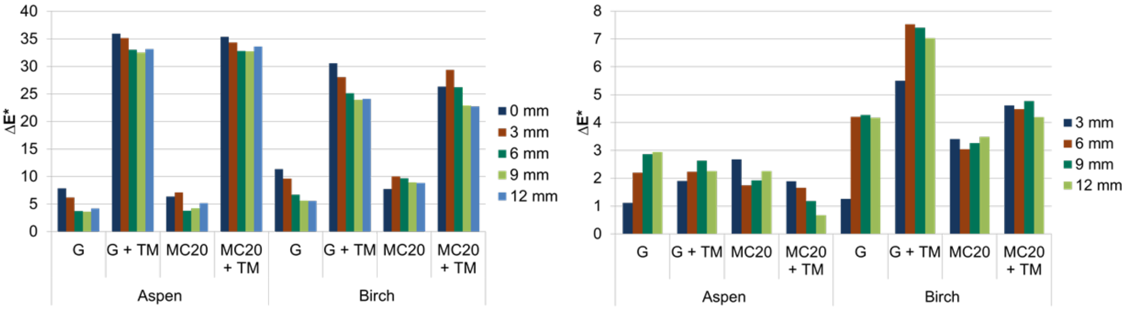

Figure 2: The colour difference (ΔE*) between unmodified, low-temperature-dried and modified wood at different depths in the direction of thickness (left) and between the surface and different depths in the direction of thickness of the low-temperature-dried and modified wood (right).

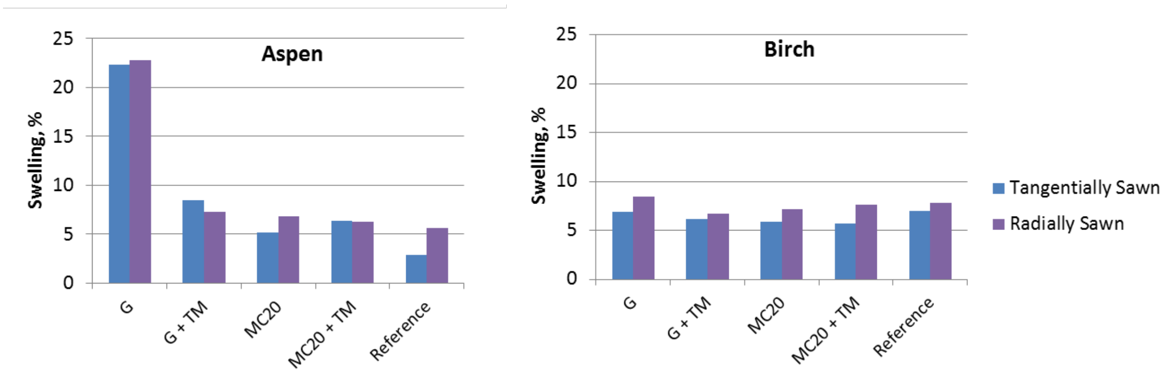

Figure 3: Swelling of thickness of modified boards during water immersion

CONCLUSIONS

We noticed that the starting phase of compression had an effect on the magnitude of densification. The colour of wood was darkest near to the most densified annual rings. Compressing green sawn timber instead of pre-dried material, and using thermal modification after compression, reduced the set recovery behaviour. Our experiments indicate that industrial scale compression of aspen and birch is possible, and problems related to set recovery of compressed wood can be decreased, though not eliminated, using post compression thermal modification.

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Evaluation of Heat Treated Veneers of Various Wood Species

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Keywords: colour changes, heat treatment, NIR, veneer.

ABSTRACT

Heat treatment is applied to wood to enhance its properties and give a higher level of functionalization to the final product (Priadi and Hiziroglu 2013). However, little information may be found relating to wood veneers on this topic. Due to their thickness, veneers need a shorter duration of heat treatment to achieve a desired colour change when compared to solid wood (Denes and Lang 2013, Feher *et al.* 2014). Apart from their uses in plywood or LVL manufacture, veneers can be used as overlaying materials for the lamination of particleboards and MDF for furniture purposes (Nazerian and Ghalehno 2011, Murata *et al.* 2013, Bekhta *et al.* 2014). Most heat treated veneers exhibit a darker appearance which allows them to replace tropical species. The aim of this study was to evaluate the effect of heat treatment on colour changes occurring in veneers of various wood species by using CIELab and NIR spectroscopy. Veneer samples, obtained from Romanian and Japanese wood species, were subjected to heat treatment in a regular oven at the same temperature level and for different span times. Colour measurements were performed according to the ISO 7724-2 standard by using a Chroma Meter Konika Minolta CR-400 device. NIR spectroscopy is a useful tool for the chemical characterisation of colour changes appearing on heat treated surfaces (Sandak *et al.* 2013). A MatrixF-Bruker Optics FT-NIR spectrometer was used for the NIR measurements. As expected, heat treatment affected the wood colour of all species. The colour responses among species varied with increasing treatment time. The FT-NIR spectra allowed a better understanding of the mechanism of thermal decomposition in the wood chemical components to be obtained. The application of heat treatment to veneers from common or under-utilized wood species could therefore enlarge their use for high value product.

INTRODUCTION

Heat treatment is applied to wood to enhance its properties and give a higher level of functionalization to the final product (Priadi and Hiziroglu 2013). However, little information may be found relating to wood veneers on this topic. Due to their thickness, veneers need a shorter duration of heat treatment to achieve a desired colour change when compared to solid wood (Denes and Lang 2013, Feher *et al.* 2014). Apart from their uses in plywood or LVL manufacture, veneers can be used as overlaying materials for the lamination of particleboards and MDF for furniture purposes (Nazerian and Ghalehno 2011, Murata *et al.* 2013, Bekhta *et al.* 2014). Most heat treated veneers exhibit a darker appearance which allows them to replace tropical species.

The aim of this study was to evaluate the effect of heat treatment on colour changes occurring on veneers of various wood species by using CIELab and NIR spectroscopy.

EXPERIMENTAL

Veneer samples with a thickness of 0.5mm made of black alder wood (*Alnus glutinosa* L.) native in Romania and Hinoki/Japanese cypress wood (*Chamaecyparis obtusa* Endl.) from Japan were used. The samples were cut into 70 mm x 70mm square shaped specimens. Altogether a total of 24 veneer samples were prepared for both species. Three groups, each of four samples were used; the first group was kept for reference. The heating process was carried out in a regular oven at 190°C for 10 and 40 minutes exposure time. Before the heat treatment, all samples were conditioned at 20°C and 60%RH.

Colour measurement

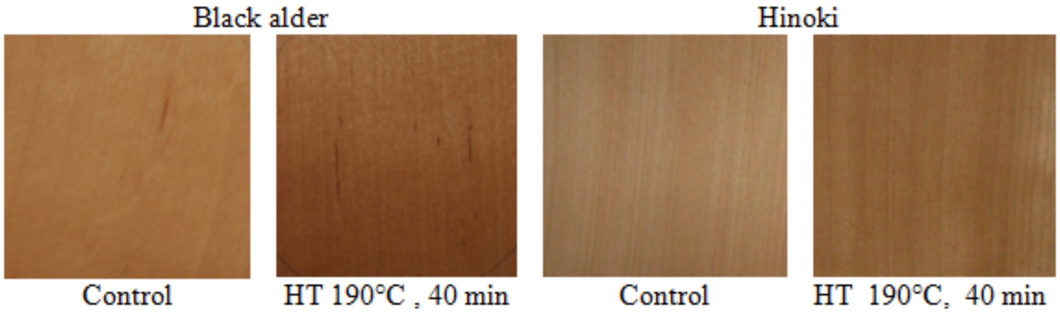
A Chroma Meter Konika Minolta CR-400 device was used for colour measurement. For each veneer sample three measurements were made under the CIELab System and according to the ISO 7724-2 standard. The L^*, a^* and b^* colour coordinates were determined both for the control group and the exposed veneers. The differences in the three colour coordinates (ΔL^*, Δa^* and Δb^*) and then the total colour change ΔE^* were calculated.

NIR measurement

A Matrix-F Bruker Optics spectrometer was used for NIR measurement. Diffuse reflectance NIR spectra ranging from 10,000-4,000cm^{-1} with a 3.85cm^{-1} interval were recorded from veneer surface. Three measurements were performed on each sample. With a view to seeing spectral variations, the second derivative was computed by gap-segment derivative (segment=7, gap=3). The correlation coefficients between heat exposure time and each absorption band were then calculated to evaluate how the heat treatment influences the chemical components. Predictive models for $L^*a^*b^*$ values were built by Partial Least Squares regression analysis (PLSR). The relationship among the $L^*a^*b^*$ values, heat treated duration and absorbance at NIR region was investigated. Data were processed by Matlab R2014a.

RESULTS AND DISCUSSION

Heat treatment affected the colour of both veneer species. L^*, a^* and b^* average values and the visual appearance of the control and heat treated samples are presented in Figure 1.



L*=70,81(1,65)	L*=57,05 (1,16)	L*=77,64 (1,15)	L*=71,65 (0,64)
a*=8,42 (0,60)	a*=10,67 (0,23)	a*=4,37 (0,78)	a*=5,63 (0,26)
b*=25,78 (0,28)	b*=23,97 (1,04)	b*=24,18 (0,52)	b*=27,44 (0,34)

Figure 1: Colour changes after heat treatment (number in parenthesis are standard deviations)

A reduction in lightness *L** for both species was noticed after the heat treatment. The degree of redness in black alder showed a significant increase when compared to hinoki, whilst the degree of yellowness for hinoki recorded the highest value among the species. Moreover colour coordinates *a** for hinoki and *b** for black alder could not be predicted because they did not change by heat treatment. It appeared that the total colour changes *ΔE** were highly influenced by the behaviour of the lightness differences *ΔL**.
Based on the correlation between several absorption peaks and heat exposure time (Figure 2), it was found that absorption due to crystalline regions of cellulose (band 6445cm^{-1}) for hinoki has a strong negative correlation, while in the case of black alder it has a weak positive correlation. The largest spectral variation was observed due to water (band 5211cm^{-1}). In the case of hinoki, a larger spectral variation was observed due to hemicellulose (band 5797cm^{-1}, band 4675cm^{-1}).

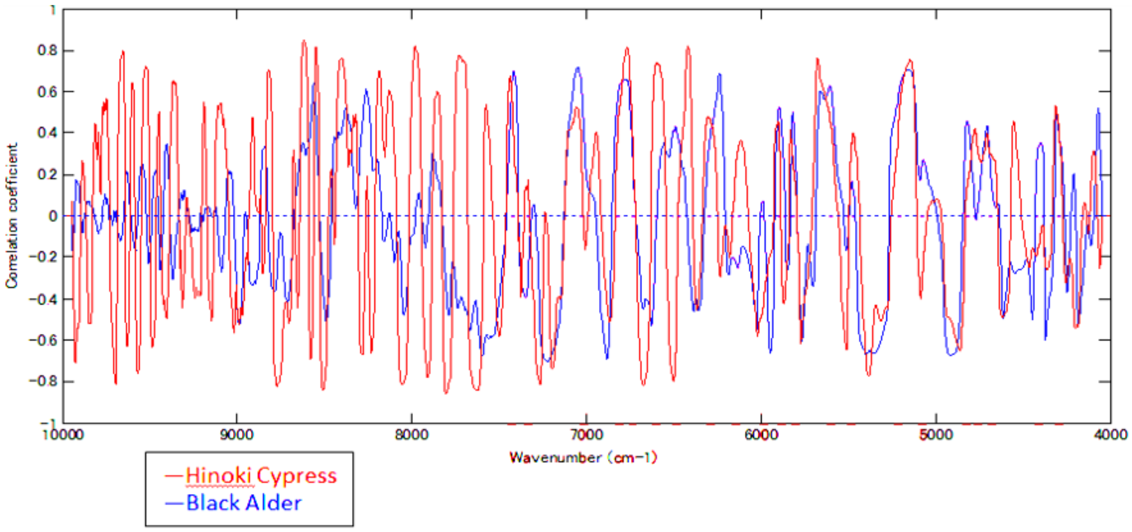


Figure 2: Correlation between NIRS and heat exposure time

As already mentioned, lightness decreased as the heat exposure increased. One of the dominant factors for the prediction of *L** was H_2O (band 7001cm^{-1}, band 5211cm^{-1}) and in case of hinoki, also hemicellulose at band 5797cm^{-1} (Figure 3).

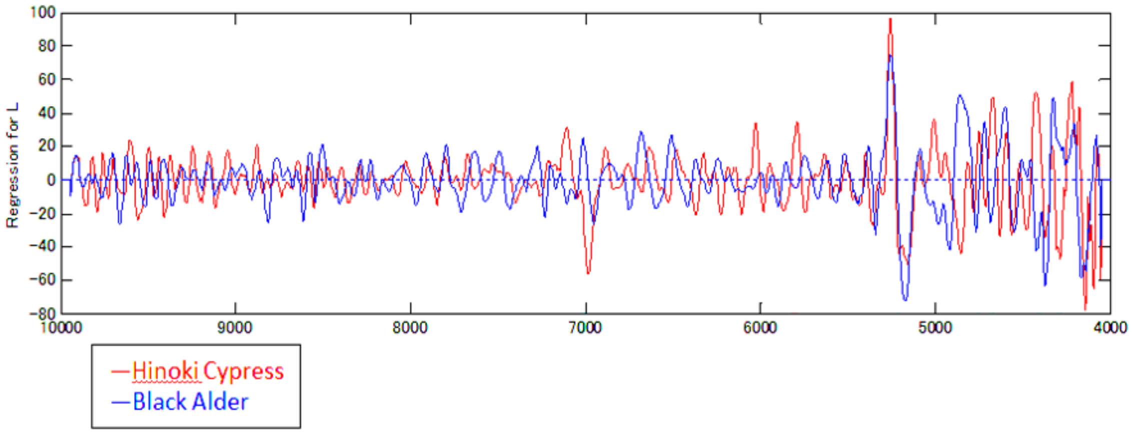


*Figure 3: Regression coefficient for L*of hinoki and black alder*

CONCLUSIONS

As expected, heat treatment affected the wood colour of both species. The colour responses among species varied with increasing treatment time. Lightness values decreased as the duration of heat treatment increased. In case of black alder veneer, although *a** value slowly increased as the duration of heat treatment increased, the relationship between heat treatment duration and *b** value was unclear. Predictive models for *L** values built from NIR spectra showed proper prediction accuracy. However, prediction models of *a** for hinoki cypress and that of *b** for black alder did not work. The results of the present study may help to clarify the relationship between colour appearance and changes in chemical components. The application of heat treatment to veneers from common or under-utilized wood species could therefore enlarge their use for high value product.

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Determination of Cracking Susceptibility of Three Thermally Modified Hardwoods by Advanced Methods

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Keywords: cracking, thermal modification, hardwoods, test method, quality

ABSTRACT

Although improved biological durability and dimensional stability are the main reasons to manufacture thermally modified timber (TMT), two of the most frequent problems in practical use are cracking and distortion. Furthermore, to assess the susceptibility to cracking could be an important part of quality assurance and factory production control (Scheiding *et al.* 2010) and a tool to predict the material performance in service. Two exposure methods were investigated to provoke crack formation under defined conditions and within a short time. A specific, four-step analysis method was established to assess the samples after exposure, considering several parameters like the amount of cracking, their size and type and the appearance of cupping. Finally, from 5 parameters a cracking susceptibility rating (CSR) value was deduced, which can be allocated to the low, medium and high cracking susceptibility of a material.

INTRODUCTION

The first reason for the development and industrial introduction of wood modification was to improve both biological durability (against wood-decay fungi) and dimensional stability. With thermal modification, the wood is often treated with very high intensities (temperatures), to reach high durability classes, comparable to durable tropical wood species, like teak or others. Although the swelling and shrinkage is reduced, the internal strength (bonding) is reduced as well and frequently to a higher extent, since cracks may be formed, when shrinkage causes tensile stress exceeding the internal strength.

EXPERIMENTAL

Boards from European beech (*Fagus sylvatica* L.) and European ash (*Fraxinus excelsior* L.) were thermally modified (TM) in a lab kiln at 200 °C under atmospheric pressure using steam as the screen gas. Hybrid poplar (*Populus × canadensis* var. Robusta) was modified in an industrial, hygrothermal process at 175 °C and 6 bar. For ash, two cutting types were considered, to assess their influence on crack formation. The material variant are summarised in Table 1.

Table 1: Material variants

Variant	HT step level [°C]	HT step duration [h]	Cutting type
TM poplar 175 qs	175	3	semi-quarter sawn
TM ash 200 qs A	200	3	semi-quarter sawn
TM ash 200 qs B	200	3	semi-quarter sawn
TM ash 200 rs	200	3	regular sawn
TM beech 200 qs	200	3	semi-quarter sawn

A first approach to a cracking test method, derived from wood-based panel testing (boiling in water + drying), was presented at ECWM7 by Direske *et al.* (2014). The size of the specimens was 140 mm x 70 mm and thickness 20 mm. Although crack formation could be induced, exposure seemed to be too harsh, compared to the conditions in use. This method was thus modified and improved. The size of the specimens was now increased to 250 mm length, 120 mm width and 25 mm thickness, to better reflect the practical dimensions of e.g. terrace decking boards. For each wood species and variant, 4 specimens were tested. For all specimens, an upper "use" face was defined, which was exposed to UV light and water spray in the QUV device and to dry air in the oven. The exposure to induce cracks was performed according to 2 principles:

Principle A used artificial weathering over 168 h (≈ 1 week) in a QUV test device according to EN 927-6. Here, specimens were exposed to cycles of water spray, elevated temperature and UV radiation. The test duration was extended by two weeks.

Principle B used complete immersion in water and subsequent drying; preliminary tests with partial immersion of one face side had not provided satisfactory. The immersion in tap water at 20°C lasted 104 h and was followed by a drying phase of 64 h in a drying lab oven at 45 C. For drying, the specimens were arranged with the lower side on a metal sheet, to simulate more one-sided drying like in service. The entire treatment duration was 168 h, as for principle A with the QUV test.

After exposure of one week (and after two and three weeks for the QUV test), the upper surfaces of all specimens were assessed visually according to EN ISO 4628-4 table 1 (five assessment classes). To assess the crack formation after the exposure, five parameters were determined as important and appropriate (Table 2):

Table 2: Parameters for crack assessment

Parameter	Unit	Assessed area	Weighting	Symbol
amount of surface cracks[a]	[-]	upper face side	1	asc
maximum crack width	[mm]	both face sides	2	mcw
maximum crack length	[mm]	both face sides	1	mcl
amount of throughout end shakes	[-]	both ends	2	aes
cupping[b]	[mm]	dished face	1	cup

[a] *according to EN ISO 4628-4 table 1,* [b] *according to EN 1310*

To describe the "cracking susceptibility" as a complex material property, these different parameters should be matched and made operable. As a first approach, the single values were standardized with 0 as the lower and 1 as the upper limit. Then, the arithmetic means of the standardized values were summarized as a "crack susceptibility rating" or CSR, weighting crack width and the amount of throughout end shakes twice, since they are considered particular important. To get an adequate scale, the sum was divided by 7 (Eqn. 1).

$$CSR = (asc + 2 \times mcw + mcl + 2 \times aes + cup) / 7 \qquad (1)$$

In a last step, the CSR range between 0 and 1 (maximum possible value) was divided into 3 rating classes, representing with CSR < 0.3 a low, with 0.33 … 0.67 a medium and with > 0.67 a high cracking potential.

RESULTS AND DISCUSSION

Using both exposure principles, A and B, crack formation was induced, as intended, as shown by the examples in Figures 1 and 2. Whereas the immersion test showed clear effects after one week, the QUV test only showed these clear effects after 2 and 3 weeks.

Generally, TM beech showed more intensive cracking than TM ash and this more than TM poplar. In contrast to the others, TM poplar showed more or less no cupping. For TM ash, the regular sawn specimens showed much more cracking than the semi-quarter sawn ones. This confirmed the findings of investigations with TMT decking boards in service.

Figure 1: TM beech 200 qs, 504 h QUV

Figure 2: TM beech 200 qs, 168 h immersion

The evaluation method, with standardizing the five assessment parameters, provided clear differences between the material variants, visible by different patterns of the materials (Figure 3).

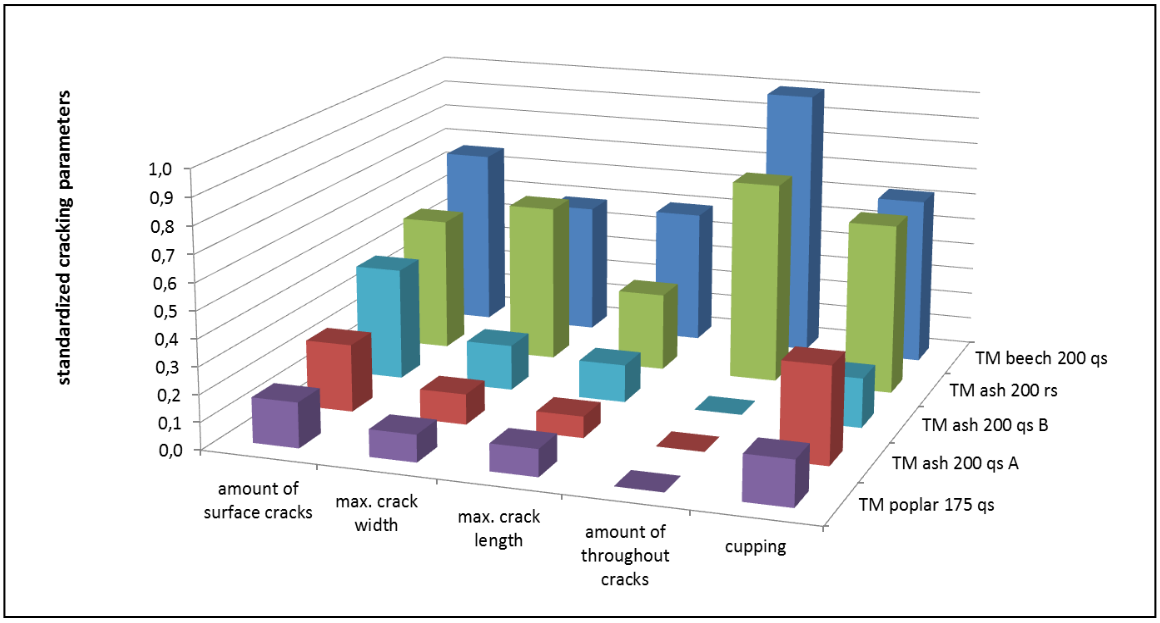

Figure 3: Standardized parameters to describe cracking susceptibility

Calculating a CSR value for every material, clear differences between the materials were determined, as shown in table 3. The cutting method had an important effect, as the TM ash 200 variants showed, where quarter-sawn wood resulted in a low CSR and regular-sawn wood a medium, but much higher CSR.

Table 3: Resulting cracking susceptibility ratings (CSR)

Variant	**CSR value (scale 0 - 1)**	cracking susceptibility
TM poplar 175 qs	0.09	low
TM ash 200 qs A	0.13	low
TM ash 200 qs B	0.15	low
TM ash 200 rs	0.59	medium
TM beech 200 qs	0.68	high

CONCLUSIONS

Two exposure principles to determine the susceptibility of wood to cracking under service conditions were applied to thermally modified hardwoods. Both exposure tests include wetting and drying phases, are easy to perform and need a short test time.
Principle A – exposure to artificial weathering according to EN 927-6 (QUV) – requires a special test device (available in some labs), but additionally provides exposure to UV radiation, thus discoloration under service conditions can be assessed as well.
Principle B – immersion test – requires simple equipment to soak and dry specimens under defined conditions, and is therefore suitable for the factory production control of a TMT producer. Whereas both partial and full immersion effected a crack formation and showed differences between the materials, complete immersion can be performed more easily without disadvantages.
TM poplar performed best, compared to TM beech and TM ash. The tests on TM ash with different annual ring orientation showed, that quarter-sawn or semi-quarter sawn cutting should be preferred, when crack formation in susceptible wood is to be avoided in practice.
The assessment presented and the calculation method provided clear differentiation between the materials and reflected the crack formation assessed visually. The methods have to be applied to further materials and be adjusted and validated.

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Applicability of Electrical Methods to Determine Moisture Content of Thermally Modified Timber

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Keywords: moisture content, electrical resistance method, capacitance method, high-frequency method, thermally modified timber, spruce, beech

ABSTRACT

The moisture content of thermally modified and untreated wood from Norway spruce and European beech was determined with two electrical methods and compared to the oven-dry method. Wood was acclimatised to three moisture levels. The results showed that both electrical methods provide acceptable data, although statistical analysis showed significant differences to the oven-dry values for most variants. The capacitance method provided more precise results, compared to the oven-dry method.

INTRODUCTION

Measurement of the moisture content (MC) of wood is an important task in the wood industry, wood trade and construction. Equilibrium moisture content (EMC) in specific climates is one suitable indicator for modification (Scheiding *et al.* 2010); thus $\mathrm{EMC}_{20/65}$ is one of the values to be determined according to CEN/TS 15679.

For MC determination, beside oven-dry method (EN 13183-1), different methods and instrument types are available. For practical conditions, the electrical resistance (EN 13183-2) and capacitance method (EN 13183-3) are typically used. In practice it is often asserted that electrical methods or devices are generally not applicable to modified timber. To clarify that, within the framework of a master thesis, MC was determined by electrical methods with untreated and thermally modified wood at different moisture levels.

EXPERIMENTAL

Wood from spruce and beech was thermally modified in a lab-sized kiln (type MAHILD MH 2000 TMT) at a treatment temperature of 205 °C over 3 h.

The specimens were stored in normal and wet climates and immersed in water. The air humidity was adjusted by storage above saturated salt solutions according to DIN 50008-1. Within the storage containers, air was circulated by a fan. The mass constancy and equilibrium moisture content, respectively, were reached after 10 weeks (storage in climate chamber) and 6 weeks (storage in water), respectively.

For each material variant, 10 replicates were tested; the MC measurement was performed once per specimen and method. Details are given in Table 1.

The technical documentation about all the devices used (as for others) does not include information about accuracy of the measurement; usually, the accuracy of the display (decimals) or the moisture range (e.g. 6-25 %, 10-50 %, 4-100 %) is indicated. Usually, an accuracy of ± 1.5…2 % up to ± 4 % is assumed.

Table 1: Experimental variants

Wood species	European beech (Fagus sylvatica L.) Norway spruce (Picea abies Karst.)
Treatment variants	thermally modified (205 °C, 3 h) untreated
Specimen size	150 mm length, 100 mm width, 20 mm thickness
Thermal modification	Lab thermo-kiln, high temperature step 205 °C over 3 h, atmospheric pressure, steam as screen gas
Climate conditions	normal climate (20/75), saturated NaCl solution wet climate (20/96); saturated KH_2PO_4 solution saturated; 21 d immersion in tab water of 20 °C
MC measurement	electrical resistance method; device: GANN Hydromette HT 65 capacitance method; device: Brookhuis FMW-B moisture detector oven dry method (103 °C)

All single data were tested statistically, using KS-test for normal distribution, F-test for homogeneity of variances and t-test for significance of population means. The level of significance was defined as 0.05.

RESULTS AND DISCUSSION

The results of the MC measurement of electrical resistance and capacitance method, compared with the oven-dry method as reference, are shown in Table 2.

Table 2: Moisture content with resistance and capacitance method and comparison to oven-dry method by difference (Δ) and significance of mean values (n = 10; F-test; alpha = 0.05)

Climate	**Material**	**Moisture content [%]**					**Significance**	
		oven-dry	**resist.**	**Δ**	**capacit.**	**Δ**	**resist.**	**capacit.**
20/75	Spruce	15.1	11.6	-3.5	15.5	0.4	x	x
	Spruce TM	8.7	6.9	-1.8	10.4	1.7	x	x
	Beech	13.2	11.2	-2	12.1	-1.1	x	x
	Beech TM	6.8	5.2	-1.6	6.3	-0.5	x	x
20/93	Spruce	19.0	16.6	-2.4	17.1	-1.9	x	x
	Spruce TM	12.3	14.0	1.7	13.4	1.1	x	-
	Beech	20.1	16.9	-3.2	21.1	1	x	-
	Beech TM	10.6	11.0	0.4	9.2	-1.4	x	x
soaked	Spruce	85.4	50.8	-34.6	78.4	-7	x	x
	Spruce TM	86.0	35.1	-50.9	78.2	-7.8	x	x
	Beech	84.8	52.4	-32.4	67.3	-17.5	x	x
	Beech TM	65.6	43.4	-22.2	67.2	1.6	x	x

Except for the values of the soaked samples, the differences in the measured values did not exceed the above mentioned expected correctness range. However, the F-test revealed a significant difference to the oven-dry value in most cases. The rejection of H_0 hypothesis (= significance) was caused by different standard deviations and too large an inhomogeneity of statistical collectives.

For dry and normal climate conditions, the capacitance method was more precise for modified spruce and beech than electrical resistance. Above 40 % MC (immersion in

water), the electrical resistance method showed better values, i.e. MC was nearer to the oven dry value than the capacitance method. The values from the resistance method for soaked samples are not usable. For very low MC below 5 %, the electrical resistance device took a long time until the displayed value was steady.
Figure 1 and 2 exemplify the MC for TM spruce and beech in the hygroscopic climates 20/75 and 20/93 (boxplots with range, median and confidence interval for $\alpha = 0.05$).

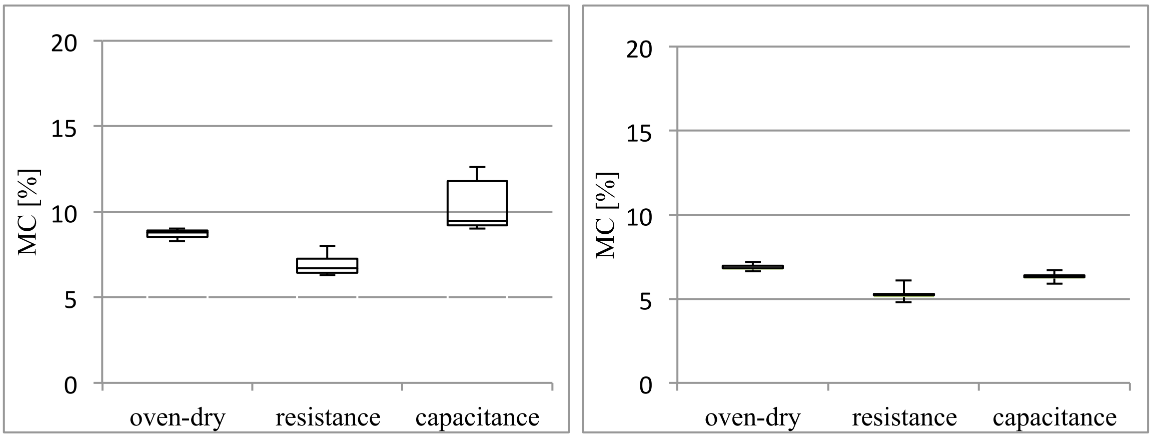

Figure 1: Moisture content (MC) of TM spruce (left) and TM beech (right) in normal climate 20/75

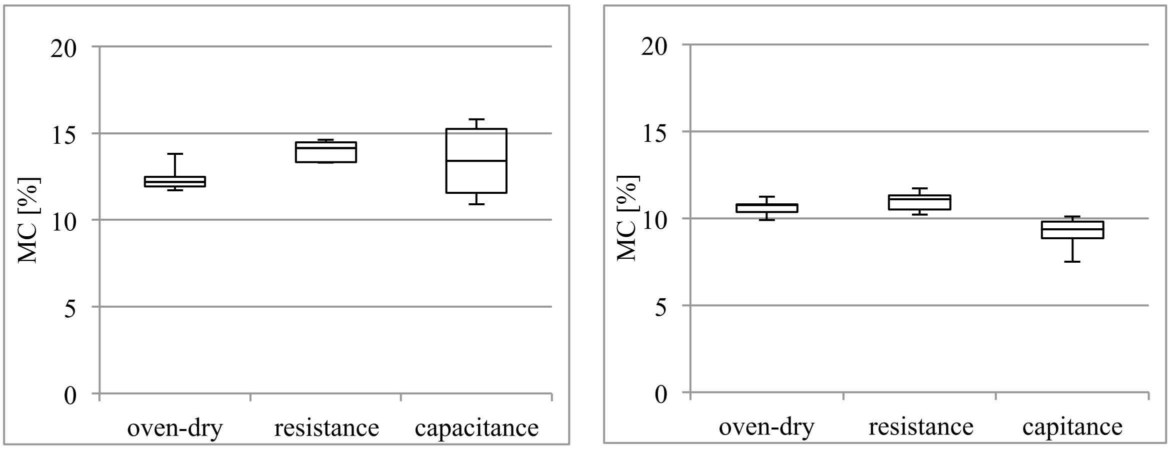

Figure 2: Moisture content (MC) of TM spruce (left) and TM beech (right) in wet climate 20/93

CONCLUSIONS

In conclusion, the capacitance method proved to be the best; the MC values were closest to the real ones, determined by the oven dry method, although in many cases the difference was statistically tested to be significant.
Both electrical methods proved to be suitable to determine (strictly speaking estimate) the moisture content of thermally modified timber.
The electrical resistance method, as the most common one used in practice, was proven to be applicable as well in the hygroscopic moisture range, i.e. below the fiber saturation point (range). Deviations between electrically determined and oven dry moisture values of modified samples were not larger than of those of untreated wood.

Above the hygroscopic moisture range, the capacitance method provided feasible values, taking into consideration that, for higher MC values, the measurement accuracy is generally decreasing with increasing MC.

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Development of Thermally Modified European Wood to Substitute Tropical Hardwood for the Use in Acoustic Guitars

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Keywords: acoustic guitars, acoustic properties, cedro, modal analysis, spruce, thermal modification

ABSTRACT

The possibility of using thermally treated Norway spruce (*Picea abies* (L.) Karst.) in the necks of high-quality acoustic guitars to substitute cedro (*Cedrela odorata* L.) wood has been studied. The heat treatments were performed at treatment temperatures between 140°C and 180°C and treatment times between 4h and 12h. The acoustic properties were determined by means of experimental modal analysis (EMA) and the mechanical properties by means of static and impact bending tests. The results show that both the acoustic and mechanical properties of spruce improve partly owing to thermal treatment, and are similar or better compared to cedro.

INTRODUCTION

The individual components of high-quality acoustic guitars: neck, sound board and fretboard, usually consist of tropical hardwoods: cedro (*Cedrela odorata* L.), rosewood (*Dalbergia latifolia*), Mexican ziricote (*Cordia dodecandra*), mahogany (*Entandrophragma cylindricum*) and ebony (*Diospyros crassiflora*). This is because of their high stiffness and dimensional stability as well as the excellent colour nuances in comparison to European wood species. Furthermore, the wood must be stored for a long period of time, sometimes for decades, to achieve suitable properties, in particular high resonance quality and reduced growth stresses, for their use in high-quality acoustic guitars (natural wood aging). In addition to the much higher costs, the availability of these 'tonewoods' is significantly reduced. According to the CITES Convention the trade in some tropical hardwoods is limited (Dietrich *et al.* 2014). Thus, there is a need to substitute materials for such applications.

Therefore, the aim of this investigation was the thermal modification (TM) of Norway spruce (*Picea abies* (L.) Karst.), to improve its acoustic and mechanical properties in line with cedro (*Cedrela odorata* L.) for substitution in high-quality acoustic guitars. Cedro or Spanish cedar is a tropical hardwood and grows from Central America to tropical South America. The wood is the traditional choice for making the neck of acoustic guitars because of its low density combined with relatively high stiffness. Hence, the choice of a substitute wood fell on spruce (softwood). Cedro is listed in the Red Data Book of the IUCN as being "Vulnerable" due to ongoing exploitation.

TM is a heat treatment procedure for wood with reduced oxygen concentration aimed primarily at improving dimensional stability and biological durability (Hill 2006). However, the mechanical properties decrease significantly at the treatment temperatures of 180°C and more usually used to improve the biological durability. There have been some papers reporting investigations into the TM of hardwood such as mulberry (*Morus* *alba* L.), birch (*Betula* spp.), aspen (*Populus tremula*) and European beech (*Fagus sylvatica* L.), using lower temperatures below 160°C (Mohebby *et al.* 2007, Biziks *et al.* 2010, Zauer *et al.* 2014). These studies show that in addition to improved stiffness and acoustic properties, strength increase owing to TM at "mild" temperatures of up to 160°C.

EXPERIMENTAL

The heartwood of untreated and TM spruce as well as untreated cedro were investigated. In all series matched boards from selected tonewood were used. The thermal treatments were conducted in a laboratory oven. The wood planks to be treated were sealed using a special thermally stable protective film to exclude oxygen. Moreover, the sealed wood packages were evacuated before transferring into the oven. The treatment temperatures differed between 140°C and 180°C and the treatment times varied between 4h and 12h.

All investigations were conducted after the specimens had equilibrated at 20°C and 65% relative humidity (RH). Raw density (DIN 52182), equilibrium moisture content (EMC) (DIN EN 13183-1), impact bending strength (DIN 52189-1), modulus of rupture (MOR) and modulus of elasticity (MOR) (DIN 52186) were determined. Furthermore, the maximum volumetric swelling of the specimens between 0% and 85% RH (DIN 52184) was determined.

The acoustic properties were determined before the destructive bending tests on the same specimens at 20°C and 65% RH. The investigations into the acoustic properties of the material were conducted using the experimental modal analysis (EMA) according to Zauer and Pfriem (2010). Using EMA, resonance frequencies, f, and the damping of vibrations, $\tan\delta$, at different own mode shapes can be determined. The latter is an important characteristic parameter for the assessment of wood for musical instruments (Bucur 2006). In addition, the sound radiation coefficient, R, (Wegst 2006), which can be calculated by means of the dynamical modulus of elasticity E' (Sproßmann *et al.* 2013) and raw density ρ of the specimens (Eqn. 1), was determined.

$$R = \sqrt{\frac{E'}{\rho^3}} \qquad (1)$$

RESULTS AND DISCUSSION

Figure 1 shows the results of the investigations presented as box plots displaying five-point summaries (median, the two quartiles and the two extreme values). It is obvious that the EMC of spruce decrease significantly owing to the TM. Although the maximum volumetric swelling of spruce decrease owing to TM, it is always higher compared to cedro. TM of spruce at 180°C for 4h leads to higher density. This is probably owing to cell-wall compression (Zauer *et al.* 2013) combined with an increase in the crystallinity index (Kubojima *et al.* 1998) at this treatment temperature. As a consequence of this phenomenon, combined with the reduced EMC, the mechanical properties: MOR, MOE and even the impact bending strength increase. The damping values decrease owing to TM up to the level of cedro, which reflects good acoustic behaviour. The sound radiation coefficient, R, of untreated spruce is significantly higher compared to cedro, but decreases slightly owing to TM. However, R is in all TM series significantly higher compared to cedro.

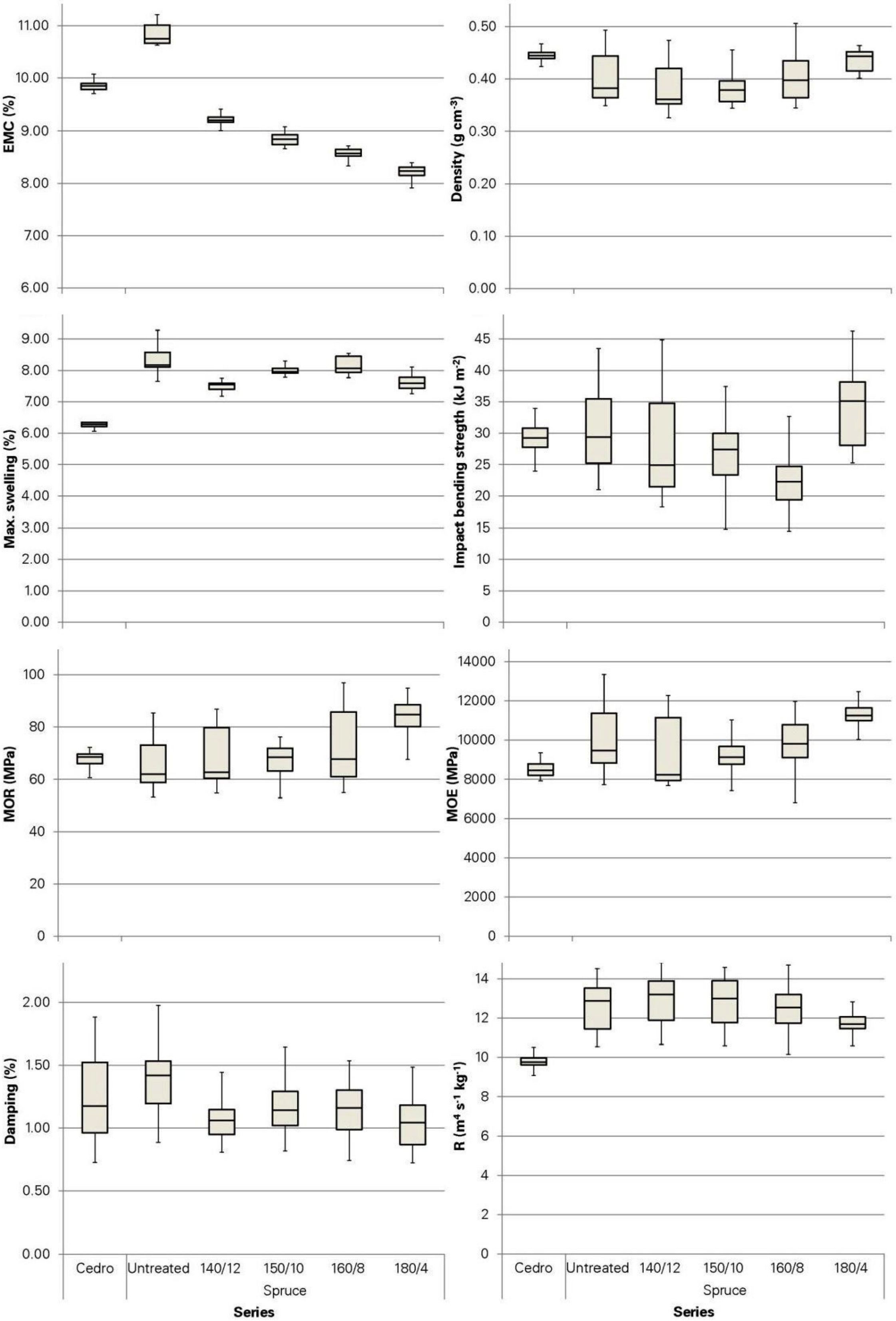

Figure 1: Comparison of the properties at 20°C and 65% relative humidity of cedro, untreated spruce and thermally treated spruce at different treatment temperatures and treatment times

CONCLUSIONS

This work has shown that it is possible to use thermally modified Norway spruce treated at relatively mild treatment temperatures in acoustic guitar necks as an alternative to cedro (Spanish cedar). In particular, a thermal treatment procedure of spruce at 180°C for 4h can be concluded to be a favourite for this application. The high dimensional stability of cedro could not be reached owing to the treatment temperatures and treatment times used.

ACKNOWLEDGEMENTS

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Dimensional Stabilization of Solid Wood Panels by Thermal Post-Treatment

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Keywords: solid wood panels, thermal modification, water uptake, deformation

ABSTRACT

The aim of this study was to enhance water repellency and dimensional stability by the thermal post-treatment of cross-laminated solid wood panels (SWP). To achieve this, three-layered Norway spruce (*Picea abies*) SWP were thermally modified in an oven at 165 °C, 175 °C and 185 °C for a holding time of 1 h. The thickness swelling (TS) and water absorption (WA) after 14 days immersion in water, the differential swelling coefficient (DS) between a normal and wet climate and the hygroscopic warping (HW) in a double climate chamber of the control and modified samples were investigated. The thermal modification (TM) decreased the TS but increased the WA. The dimensional stability under different hygroscopic moisture conditions was improved.

INTRODUCTION

Multilayered SWP are hardly used for cladding. One reason is the extreme partial climatic stress they are exposed to. By transverse gluing of the layers, swelling is substantially reduced in the plane of the panel compared to swelling perpendicular to grain of solid wood. The DS of SWP is slightly higher than that of solid wood parallel to grain, and significantly lower than perpendicular to grain (Popper *et al*. 2004). High internal stresses because of the differences in swelling and shrinkage, causes cracking perpendicular to grain when the tensile strength is exceeded.

By TM, dimensional changes in wood can be reduced due to degradation of the hydrophilic components. Investigations by Stötzel and Beikircher (2007) and by Weber and Krug (2009) showed an improvement in the dimensional stability of SWP by thermal pre-treatment of the solid wood. The effects of thermal post-treatment on SWP were less of a focus.

EXPERIMENTAL

Within this study, the reactions of 19 mm SWP made from Norway spruce to changing hygroscopic moisture conditions and liquid water were investigated. The panels were modified in a lab kiln at 165 °C, 175 °C and 185 °C under atmospheric pressure; untreated wood was considered for comparison. The SWP were placed in layers between gas-tight, temperature and corrosion resistant and highly thermally conductive sheets.

After thermal treatment, the specimens were stored in a standard climate of 20 °C and 65 % rH (20/65) until mass constancy was achieved. To evaluate changes in liquid water uptake, specimens of 50x50 mm² were cut. The specimens were water soaked for

14 days. The mass and the thickness were measured before and after to calculate WA and TS.

To assess the reaction to alternating hygroscopic moisture conditions, the DS parallel to grain was measured. After reaching constant mass, the length of the specimens (300x50 mm^2) was measured and they were stored in a humid climate of 20°C and 85% RH. After again reaching constant mass, the length was measured. From the change in length and the difference in humidity (20 % RH), the DS was calculated.

Furthermore, the HW of samples stored for 14 days between two climates in a double climate chamber with a moisture gradient of 50 % RH was measured. This shows the deformation of panels, because of moisture changes by simultaneous exposure to two different climates on both panel surfaces. The edges of the specimens (500x500 mm^2) were sealed. The SWP were positioned in a partition wall between two climatic chambers; thus the specimens could change shape without hindrance. The climate in one chamber was 20°C and 85% RH and in the other one it was 20°C and 35% RH. On the first day, the measurement (six positions) was carried out after 2, 4 and 6 hours and thereafter every 24 hours for two weeks. From these data, the dimensional changes were calculated, related to a length of 1 m in horizontal, vertical and diagonal directions relative to the production direction of the panels.

To evaluate the effect of the TM, an analysis of variance (ANOVA) was conducted using the statistical software OriginPro 9.1G. All hypotheses tests were carried out at a 95 % confidence level. Significant differences are marked in boxplots. The null hypothesis was that the TM had no effect.

RESULTS AND DISCUSSION

The investigations revealed significant differences between untreated and thermally treated SWP in reaction to moisture and liquid water. Table 1 provides an overview of the results of this study.

Table 1: Results of tests

Properties			**untreated**	**165 °C**	**175 °C**	**185 °C**
Moisture content at 20/65 [%]; n = 6		$\bar{x}$	11.08	8.96	8.95	8.42
		s	0.27	0.47	0.24	0.08
Differential swelling coefficient parallel to grain [%/%]; n = 6		$\bar{x}$	0.028	0.022	0.016	0.009
		s	0.009	0.003	0.005	0.002
14 days storage in water; n = 12	thickness swell [%]	$\bar{x}$	6.90	5.63	4.86	4.79
		s	0.68	0.28	0.38	0.58
	water uptake [%]	$\bar{x}$	76.62	86.89	87.75	87.63
		s	6.56	6.89	6.01	10.79
Deformation after 14 days between two climates; n = 4	horizontally [mm/m]	$\bar{x}$	11.97	11.68	9.81	9.60
		s	0.65	0.92	1.55	2.27
	vertically [mm/m]	$\bar{x}$	7.62	6.39	5.53	4.56
		s	1.61	0.79	0.85	0.59
	diagonally [mm/m]	$\bar{x}$	9.79	8.92	7.64	7.03
		s	1.17	0.51	0.85	1.03

After 14 days storage in water, the modified specimens had a significantly lower TS, compared to the untreated reference (Figure 1A). Not surprisingly, the TS decreased with increasing high-temperature (HT) treatment level. However, it was also found that an increase in temperature from 175 °C to 185 °C had no further effect on TS.

In contrast to TS, the WA was significantly higher after TM (Figure 1B). The statistical analysis showed no significant difference between the three different HT levels. TM is expected to reduce water absorption due to hemicellulose degradation (Korkut *et al.* 2012). However, the results in the present paper do not meet this expectation in the case of severely heated wood. It is possible that the increased porosity in such samples causes opposite behavior. Boonstra (2008) and Zauer (2011) indicated the formation of larger pores, micro-cracks and opening of bordered pits after TM. This provides more available internal space for water adsorption. Investigations by e.g. Metsä-Kortelainen *et al*. (2006) described an increase in WA below a HT-level of 200 °C.

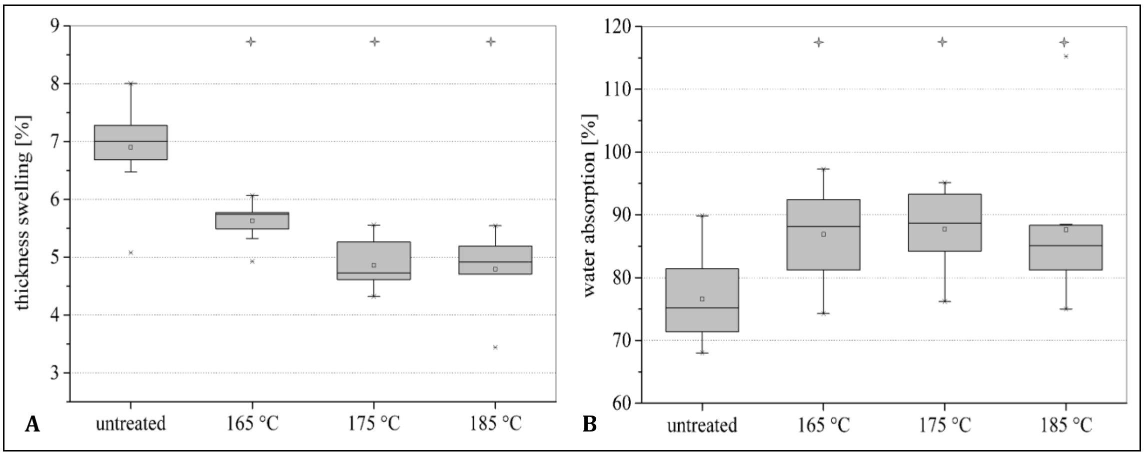

Figure 1: Effect of TM on the TS (A) and WA (B) of SWP after 14 days storage in water (sign. difference to untreated reference p<0.05 are marked; n=12)

Figure 2A shows the results of the dimensional stability test in the fiber direction of untreated and thermally modified SWP according to an increase in the relative humidity by 20 %. While the relative humidity rose from 65 % to 85 %, the length of the specimens increased. With increasing treatment temperature, the DS decreased. A significant difference was observed between the untreated and the modified SWP, unless it was at the lowest HT level. The two high HT levels improved the dimensional stability. The values are much lower than the 0.03 %/%, usually given for SWP (Popper et al. 2004). There was no statistical difference observed between these two treatments.

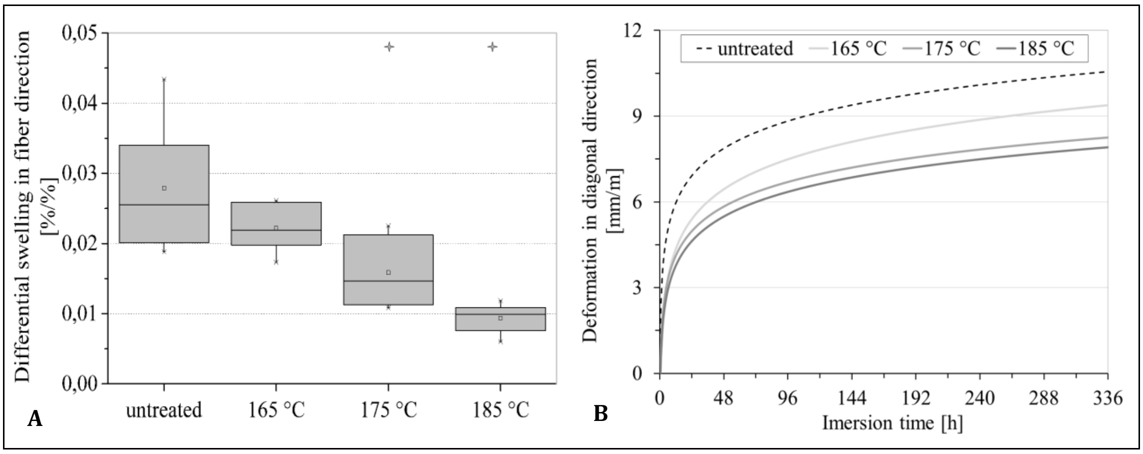

Figure 2: Effect of TM on DS (A) after rose of rH from 65 % to 85 % (sign. difference to untreated reference p<0.05 are marked; n=6) and HW (B) after 14 days between two climates (20/35 and 20/85)

Similar results as for TS and DS were indicated for the HW. The warping and cupping is due to changing moisture gradients in the material, which is positioned between a dry (20/35) and a wet (20/85) climate. However, since the thermally treated variants have a much smaller capacity to shrink and swell due to the aforementioned thermal destruction of hydroxyl groups, the dimensional changes are also less. The lowest HW was found at a HT level of 185 °C (Table 1). Figure 2B shows the variation of deformation in the diagonal directions to the cover layer.

CONCLUSIONS

With the thermal post-treatment method of Norway spruce SWP presented, it is possible to improve the moisture related properties of thermally modified variants, in comparison to untreated ones. The dimensional stability, in particular, was improved. The results indicate that a temperature of 175 °C is most suitable for improving the dimensional stability. Below this (165 °C), the effects are often very low, compared to the reference, and above (185 °C) there are hardly any additional improvements.

It was found that a thermal post-treatment will improve the dimensional stability of SWP against water vapour and liquid water. From this result lower internal stresses and a reduced risk of crack formation. This makes it possible to fulfill the high demands for cladding with thermally modified SWP.

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Chemical Changes in Mild Thermal Treatment of Larch: To What Extent Do They Differ from Full Thermal Modification?

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Keywords: thermal modification, chemistry, FTIR, GC-MS, process control

ABSTRACT

The chemical changes due to a mild thermal treatment under steam, developed in Wales to enhance the machinability and aesthetic properties of larch timber, have been investigated. While thermal modification processes conforming to DD CEN/TS 15679 (conducted at 160°C or above) are widely used, and their chemistry well explored in the literature; the chemical processes active in the less commonly used thermal treatment range 120 to 180°C (sometimes considered artificial aging) are less fully quantified. The onset of hemicellulose degradation, liberating acetic acid to further catalyse degradation, is the main phenomenon discussed in the literature. Some limited lignin degradation is recognised at the higher end of this temperature range. The observed changes in machining quality are likely to relate not only to the degradation of hemicellulose, but also to the volatilisation and re-distribution of terpenes and resin acids. This paper reports a series of small scale experiments designed to quantify and monitor the changes in chemistry, and changes in distribution of chemical extractives. These results are compared with studies conducted on wood samples selected from commercially produced batches of thermally modified larch timber. FTIR-ATR spectroscopy revealed a more complex set of changes than is generally reported. The drying of resin pockets was characterised by a reduction in carbonyl at 1721 cm^{-1}, while large differences were seen in the carbonyl absorption (1738 cm^{-1}) for some samples of treated wood, in other samples a decrease was seen, as expected. This led to proposal of different reactions dominating in the heartwood, the sapwood or the transition zone. Resin samples from resin pockets in treated and untreated wood were dissolved in methanol for GC-MS analysis. Solvent extraction of samples of commercially produced Welsh larch was also conducted, allowing GC-MS analysis of the extractive composition. Terpene content and the degradation products of hemicellulose and lignin were observed. Trends in the distribution of these components were seen, in particular, there were distinct differences in the concentration of extracts such as 5-(hydroxymethyl)-2-furfuraldehyde with the region of the tree stem.

INTRODUCTION

A thermal modification system with options for mild, or moderate, levels of transformation of the timber, has been developed for Welsh grown timbers, which tend to be faster grown than the equivalent species from their natural range. One of the most significant improvements resulting from the mild treatment is the drying of resin pockets within the timber, which reduces problems with sawing, finishing and handling the timber. The surface texture of modified larch has higher quality and lower roughness than untreated larch timber after planing or machining operations. A chemical investigation of the processes occurring during treatment has been undertaken. Larch resin in fast grown timber may be a significant problem, especially in the juvenile and pith regions of the bole – preventing use in high quality applications. However, when the resin is dried or cured by thermal processes, this timber may be used in many products.

This paper reports several studies of the chemistry of larch resulting from mild thermal treatment under steam. These include the composition of the natural larch resin, and the extractives obtained from untreated Japanese larch (*Larix kaempferi*), and equivalent timber which had been subjected to a mild thermal modification (using a treatment phase of 4 hours at 190°C). Fuller details of the treatment, including the definition of treatment phase (set temperature of the kiln) and treatment zone (duration above a specified threshold temperature) have been reported in Spear *et al.* (2015). The mild thermal treatment has been developed to maximise the beneficial effects in machining and handling the timber, including the reduction of problems due to resin exudation.

METHODS

GC-MS

Oleoresin from untreated Japanese larch was sampled for analysis by gas chromatography-mass spectrometry (GC-MS) using dichloromethane as solvent. A Perkin Elmer Clarus with a VF5 column. TurboMass Software, and the NIST Library were used together with literature values (Mills 1973, Babushok *et al.* 2011) to confirm identification of compounds. Resin found in resin pockets of thermally treated larch from the same source was also sampled, to determine changes in composition resulting from the thermal treatment procedure. Note that the resin acids were not expected to be observed by this sample preparation method, however the mono-, sesqui- and diterpenes with lower polarity were well separated for comparison.

FTIR-ATR spectroscopy

Samples of commercially treated larch were observed in attenuated total reflectance mode using a Thermo Nicolet 8000 FTIR fitted with a Pike GladiATR Vision.

Extraction followed by GC-MS

Milled wood powder from commercial treatments was soxhlet extracted using 4:1:1 solution (toluene:methanol:acetone v/v) then recovered by rotary evaporation. The residue was then dissolved in methanol for GC-MS analysis.

RESULTS AND DISCUSSION

GC-MS of resin

The GC-MS of larch oleoresin (Figure 1a) reveals three significant groups of compounds: monoterpenes, sesquiterpenes and diterpenes. Due to the different levels of functionalization on the terpenoids, some sesquiterpenoids elute later, at similar times to the diterpene fraction. When the same resin was subjected to a DSC run to simulate the conditions during the drying day (Day 1) of the thermal treatment process (which has a hold period at 120°C), the profile of compounds was altered. It was seen that monoterpene content decreased (5.13, 6.04 and 7.68 min peaks were negligible), and that the faster eluting sesquiterpenes such as germacrene and cadinene (peaks near 17 min) had been driven off by the heat Figure 1b).

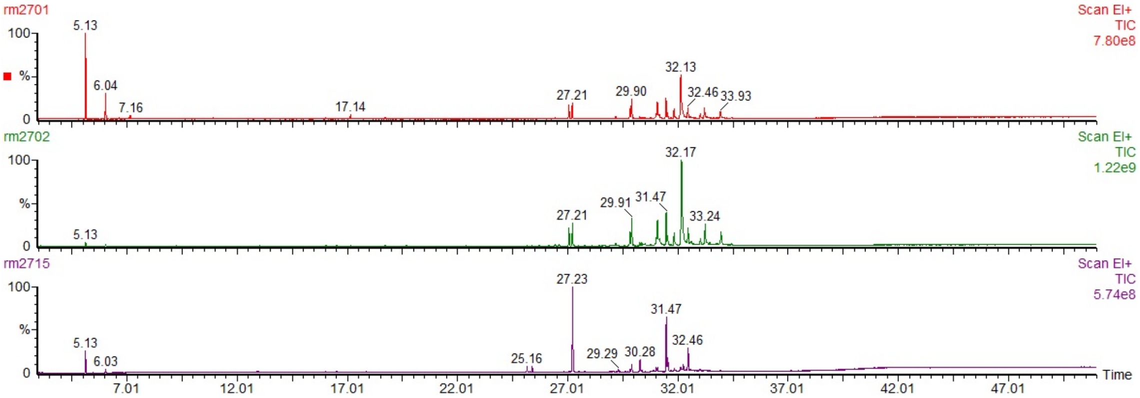

Figure 1: Gas chromatographs of (a) Resin A, (b) Resin A after DSC cycle which simulated pre-treatment of timber, and (c) a resin pocket within plank 8D from Run C

When a sample of resin was taken from a resin pocket within a thermally treated plank, the chromatograph took a different form (Figure 1c). A small quantity of the α- and β-pinene monoterpenes remained, however the cluster expected at 17 min was depleted, and the proportions of diterpenes and sesquiterpinoids seen between 26 to 32 minutes had changed, revealing three dominant components: epimanool (27.23), and two diterpene acetates (31.47 and 32.46). Analysis of the mass spectra for the 27.23 peak in untreated resin and in the treated resin pocket, revealed differences, which hint at overlapping peaks, with structural differences. In addition, many terpene peaks had been reduced or eradicated, such as thunbergene (27.06 min) and isopimaric acid (32.13 min).

FTIR of wood

In experiments where samples were scanned prior to treatment then re-scanned after thermal modification, relatively small changes were observed in the wood itself, but larger differences were seen in the resin pockets. Carbonyl absorptions at 1721 cm^{-1} and 1230 cm^{-1} were lost at a relatively low temperature of 140°C. This is likely to relate to the loss of resin acids from the oleoresin during its volatilisation.

In samples cut from planks treated in the thermal modification oven, the resin pockets again showed these characteristic changes. The wood itself revealed different spectra, depending on sample location in the sapwood, the heartwood or the transition between sapwood and heartwood. There was an increase in carbonyl absorption at 1738 cm^{-1} which appeared to correlate with a specific colouration of the timber in the transition zone.

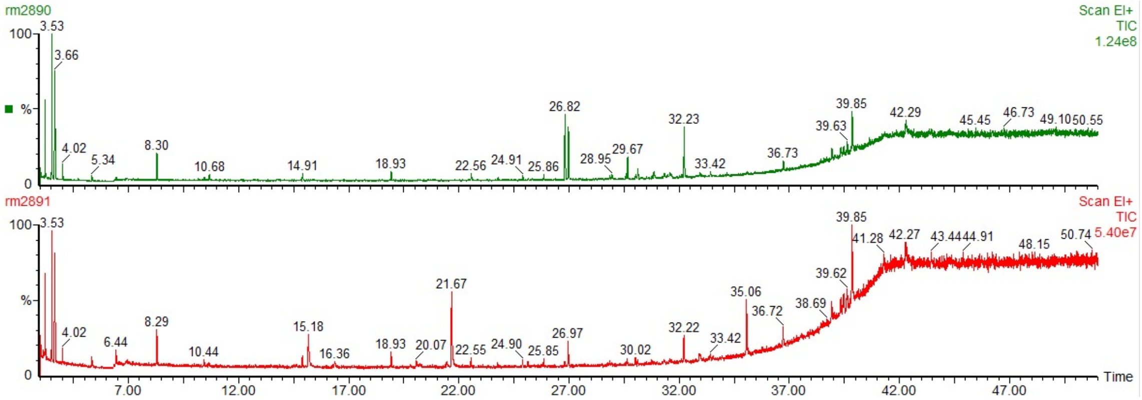

Figure 2: Chromatographs from treated larch timber 4:1:1 extract from plank 8E4 which received the full moderate intensity treatment

GC-MS of extractives

GC-MS of the 4:1:1 extractives of untreated and larch from the drying day only showed relatively minor changes (Figure 2a), with many of the terpenes still present. After thermal modification however, the evolution of new peaks such as vanillin and 3-(4-hydroxy 3-methoxyphenyl) 2-propenal (Figure 2b) occurred. Various phenyl propane derivatives with characteristic fragmentation patterns, but poor matches to the spectrum library, were also detected. 5-(hydroxymethyl)-2-furfuraldehyde and the methyl ester of homovanillic acid were detected in samples from selected regions of the treated wood.

CONCLUSIONS

The chemical changes in larch timber during mild and moderate thermal modifications have been investigated using GC-MS and FTIR-ATR. The process is a combination of the volatilisation of oleoresin components and the onset of mild acid-catalysed thermal degradation of the hemicelluloses. In this intermediate state, differences in reaction products were seen to correlate with sapwood versus heartwood regions of the tree, and a fuller explanation of these phenomena will be reported elsewhere.

The study was driven by an interest in observed changes in machining quality, which are likely to relate to the mild nature of the hemicellulose degradation, but also to the volatilisation and re-distribution of terpenes and resin acids. The results of the GC-MS and DSC work have been used in fine tuning the thermal modification schedule for mild treatment to optimise resin hardening effects and minimise strength changes in the timber.

ACKNOWLEDGEMENTS

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Modification of Wood by Cold Pressure and Heat-Treatment, and LVL Production

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Keywords: colour difference, shrinkage, heat-treatment, cold pressing, laminated veneer lumber, mechanical properties

ABSTRACT

The effect of cold pressing and then heat-treatment on the physical, mechanical, and morphological properties of birch (*Betula platyphylla* var. *japonica* Hara) and maple (*Acer mono* Maxim.) woods was investigated. For this, 50 mm thick lumbers were cold pressed to a 35 mm target thickness (30% of control lumber) in 5 min. Then, the cold pressed lumbers were heat treated in a kiln at 180 °C for 6, 12, 24, or 48 h. To increase the utilizability of the modified wood, laminated veneer lumber (LVLs) was produced from the veneers prepared from the modified lumbers. Each LVL sample consisted of 5 layers which were respectively 48 h-, 24 h-, 12 h-, and 6 h-treated veneers and untreated veneer (from the top layer to the bottom layer). The dimensional stability of the wood samples was significantly improved by cold pressing and heat-treatment. The mechanical properties of the modified wood were considerably higher than the untreated wood. The bending strength and modulus of elasticity of the LVL made from the modified maple wood were better than untreated maple wood. However, this was not observed for the modified birch wood LVL.

INTRODUCTION

Heat-treatment is a process that improves wood performance and leads to improved water repellency, reduced shrinkage and swelling, higher decay resistance, reduced extractive contents, lower equilibrium moisture content and increased thermal insulating capacity, which might prolong the service life of furniture product (Militz 2002, Hill 2006). It is well known that heat-treatment decreases the mechanical properties of wood (Yildiz et al. 2006). For this reason in this study, we increased the density of the wood samples by cold pressing before heat-treatment. The physical, mechanical and colour properties of solid wood and laminated veneer lumber (LVL) manufactured by cold pressing and then heat-treatment were investigated. The effect of heat-treatment duration on the anatomical structure of the cold pressed wood samples was also investigated using scanning electron microscope (SEM) images.

EXPERIMENTAL DETAILS

Birch (*Betula platyphylla* var. *japonica* Hara) and maple (*Acer mono* Maxim.) trees were harvested in Taebaek Samcheok, Kangwon in the Rebuplic of Korea. The tree ages and diameters at breast height were 32 and 39 cm for the birch and 30 and 42 cm for the maple, respectively. First, 50 mm thick lumber samples were cold pressed to a 35 mm target thickness (30% of the control lumber) in 5 min. Then the cold pressed lumber samples were heat treated in an electric kiln at 180 °C for 6, 12, 24, and 48 h. To increase the utilizability of the modified wood, the LVL samples were produced from 4 mm thick veneers prepared from the heat treated lumber using a veneer saw. Each LVL sample consisted of 5 layers which were respectively 48 h-, 24 h-, 12 h-, or 6 h-treated veneers and untreated veneer (from the top layer to the bottom layer) (Fig. 1f). PVA adhesive was spread at a rate of 250 g/m^2 on a single bonding surface of the veneers using a laboratory manual cylinder. After applying the adhesive, the five veneers were placed with their grain directions parallel to the grain direction of the neighbouring veneers. The LVL mats were cold pressed at 1 MPa for 24 h using compression clamps. The physical and mechanical properties of the wood and LVL samples conditioned at 65% relative humidity and 20 °C were determined according to Korean Standards. An outline of the wood modification process and the production of the LVL samples is presented in Figure 1.

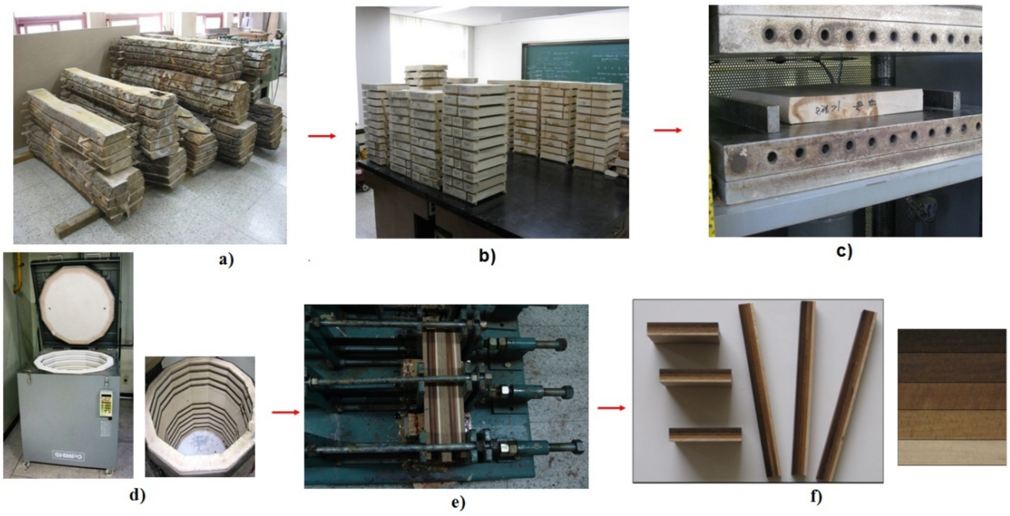


Figure 1: The production of experimental LVL samples

RESULTS AND DISCUSSION

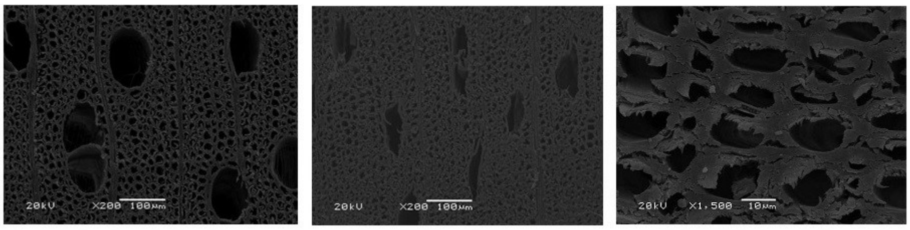
The physical, mechanical and colour properties of the control, cold pressed, and heat treated wood samples are presented in Table 1. Cold pressing before heat-treatment considerably reduced the shrinkage of the specimens and increased their densities. For example, as the thickness of birch wood decreased from 50 to 35 mm, the shrinkage rate (green to oven dry) decreased from 17.1 to 12.9%. A similar result was found in the samples of maple wood. The decrease in the shrinkage ratio of the birch samples was higher than that of the maple samples when the samples were cold pressed. The shrinkage rate of the cold pressed wood samples considerably decreased with increasing heat-treatment time (Table 1). For example, as the heat-treatment time of the cold pressed samples increased to 48 h at 180 °C, the tangential shrinkage ratio (green to oven dry) of the cold pressed birch wood samples greatly decreased (12.9 to 6.79%).

The mechanical properties of the cold pressed samples were significantly higher than those of the unpressed control samples. This was mainly attributed to the increased density of the cold pressed samples. The compressive strength, bending strength, and modulus of elasticity in bending of the wood samples decreased with increasing heat-treatment time. The primary reason for the strength loss is the degradation of hemicelluloses, which are less stable to heat than cellulose and lignin. (Yildiz et al. 2006). Although the mechanical properties of the cold pressed wood samples were negatively affected by increasing heat-treatment time, the compressive strength and the bending strength of the birch and maple samples treated at 180°C for 6 or 12 h were better than the unpressed control samples (Table 1). Apart from birch wood, the compressive strength and modulus of elasticity of the maple samples treated at 180°C for 48 h were better than those of the unpressed control samples. The colour differences among the wood samples significantly increased with increasing heat-treatment time (Table 1).

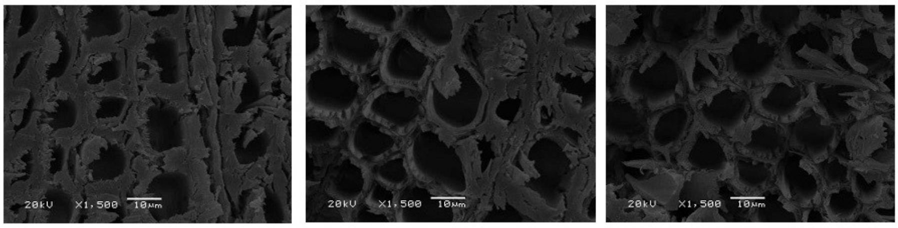
Table 1: The physical and mechanical properties of un-pressed, cold pressed, and cold pressed and then heated wood samples.

Cold pressed wood species	Heat-treatment		Density	Shrinkage (%)		CS (//)	MOE	BS	Colour difference			
			(g/cm^3)	Green to air dry	Green to oven dry	MPa	MPa	MPa	L*	a*	b*	ΔE*ab
				(Tangential)								
Birch (Betula platyphylla var. *japonic* Hara)	Unpressed wood		0.76	10.20	17.10	46.2	7616	76.3	-	-	-	-
	Pressed wood		0.89	7.89	12.90	53.4	8979	96.2	79.1	9.3	20.7	-
	Pressed wood 180°C	6 h	0.71	7.60	9.34	52.8	8006	90.3	55.0	21.0	22.4	24.4
		12 h	0.69	6.76	7.85	52.4	7583	77.1	48.5	18.4	21.6	30.8
		24 h	0.67	4.56	6.93	41.6	7253	76.5	39.9	20.2	17.0	37.5
		48 h	0.66	4.42	6.79	41.0	6978	51.4	35.8	15.7	13.3	44.0
Maple (Acer mono Maxim.)	Unpressed control		0.78	7.00	8.47	41.9	6526	78.2	-	-	-	-
	Pressed control		0.84	6.92	7.80	47.9	8607	90.6	6.5	12.6	20.4	-
	Pressed wood 180°C	6 h	0.83	6.90	7.69	47.5	8171	89.5	0.0	22.1	22.3	26.8
		12 h	0.73	6.00	6.20	45.8	7945	87.8	1.9	22.8	19.1	30.8
		24 h	0.73	4.51	5.57	43.6	7406	72.5	5.9	24.5	14.6	34.1
		48 h	0.71	4.01	5.20	43.0	7006	70.2	6.8	18.5	15	40.2

* *CS: Compressive strength parallel to grain. MOE: Modulus of elasticity in bending. BS: Bending strength.*
L: Lightness. a* (green-red) and b* (blue-yellow): Two chromatic coordinates. ΔE*ab: Colour difference.*



(A) Pressure before (B) 30% (35mm) Pressure (C) Heat treatment (180 °C 6 h)



(D) Heat treatment (180 °C 12 h) (E) Heat treatment (180 °C 24 h) (F) Heat treatment (180 °C 48 h)

Figure 2: Scanning electron micrographs (SEMs) of control, cold pressed and then heat treated birch (Betula platyphylla) wood heat-treatment

The bending strength and modulus of elasticity of the LVL samples manufactured from the veneers prepared from cold pressed and heat-treatead maple wood were found to be higher than those of the unpressed control LVL samples, however, this not observed for the LVL made from birch wood (Table 2). The bottom layer of the LVL samples consisted of the untreated veneer while the top layer consisted of the heat treated veneer treated at 180 °C for 48 h. The critical tension zone in LVL is much more important than the compression zone. For this reason, the heat treated veneers, particularly with high temperature and long duration, were positioned near the top layer.

Table 2: The physical and mechanical properties of the LVLs produced from the modified wood

Wood species	Arrangement of 5 veneers in the LVL (from top to bottom)	Density	Delamination ratio after water soaking at room temperature (24 h)		Bending properties MOE	BS
		(g/cm³)	Layer	%	MPa	MPa
Birch (Betula platyphylla var. *japonica* Hara)	180 °C – 48 h	0.74	1	5.7	6641	73.2
	180 °C – 24 h		2	0.4		
	180 °C – 12 h		3	2.1		
	180 °C – 6 h		4	7.1		
	Control (cold pressed veneer)		All layers	13.3		
Maple (Acer mono Maxim)	180 °C – 48 h	0.79	1	5.5	6968	78.7
	180 °C – 24 h		2	0		
	180 °C – 12 h		3	1		
	180 °C – 6 h		4	6.3		
	Control (cold pressed veneer)		All layers	14.5		

MOE: Modulus of elasticity in bending. BS: Bending strength.

CONCLUSIONS

It appears that cold pressing can be used as a potential approach to enhance mechanical properties of the heat treated birch and maple woods so that they can be used more efficiently during their service life without having any mechanical and dimensional movement problems. The dimensional stability and mechanical properties of low quality woods can be improved by using cold pressing and then heat-treatment

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Surface Properties of Thermally Modified Wood Floorings

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Keywords: interior floorings, surface properties, thermal modification, wood

ABSTRACT

Thermally modified wood (TMW) surfaces appear very attractive and are therefore ever more frequently used in floorings. Positive changes in properties as a result of thermal modification, like improved dimensional stability, reduced equilibrium moisture content, reduced water vapour and liquid water permeability, are frequently used as an important argument for the application of these products in everyday life. In order to protect and maintain their initial appearance, wood floors are regularly surface finished. The finishes most often used in floor coverings include UV curing varnishes, combinations of oils and waxes as well as classic solvent borne and water borne varnishes. The aim of this work was to examine the influence of the substrate as well as the efficiency of the coating material on the surface properties of TMW. For experimental purposes, samples were prepared with the following variables: wood species (oak, beech and ash), modification process (unmodified and TMW), as well as finishing system (uncoated, UV varnish, oil, UV oil). The material for testing was commercially heat treated by a local parquet manufacturer at 210°C in a water vapour atmosphere. Laboratory tests included film thickness measurements, scratch resistance, slip resistance and resistance to chemical agents. The results show relationships between all the variables tested and the surface resistance of TMW. Generally, surfaces protected with UV curing varnish exhibit better properties. However, both UV curing oil and oxidative oil which form a thin protective layer of 18 to 22 µm, showed very good resistance to chemical agents and slip resistance. Despite the fact that UV oil and oxidative oil showed similar results on wood flooring elements, a question that remains is how to ensure regular maintenance and repair of these products.

INTRODUCTION

An array of testing methods simulate the traffic loads on lacquered surfaces in use. These are in connection with a number of mechanical, physical and chemical actions that wood flooring surfaces must resist in order to retain their originally designed appearance and function.

The first indicator of wear is the loss in gloss, while prolonged abrasive action leads to a reduction in film thickness and eventually to its total disappearance.

Basic indicators for the quality of lacquered wood flooring surfaces are adhesion, resistance to wear, elasticity, impact resistance, scratch resistance, slip resistance and resistance to various chemical agents. The testing of these properties are mostly covered by relevant standards, but not all of them are suitable for testing surfaces protected with oils and waxes.

Thermally modified wood (TMW) surfaces appear very attractive and are therefore frequently used in floorings. Positive changes in properties as a result of thermal modification, like improved dimensional stability, reduced equilibrium moisture content, reduced water vapour and liquid water permeability, in combination with uniform darker shades are frequently used as an important argument for the application of these products in everyday life (Arnold 2007, Jämsä and Viitaniemi 2001, Živković *et al.* 2008, Sundquist 2004). In order to protect and maintain their initial appearance, wood floors are regularly surface finished. The most frequently used finishes in floor covering include UV curing varnishes, combinations of oils and waxes, and classic solvent borne and water borne varnishes.

The aim of this work was to examine the influence of the substrate as well the as efficiency of the coating material on the surface properties of TMW

EXPERIMENTAL

Parquet elements of oak (*Quercus robur* L.) (O), beech (*Fagus sylvatica* L.) (B) and ash (*Fraxinus* L.) (A) unmodified and thermally modified wood (160/212) factory prefinished with UV varnish (UVL) and UV oil (UVO) were selected for the experiment. Additionally, an oxidative two component oil (60 g/m^2) in combination with hardwachs oil (80 g/m^2) was applied as a third coating system (O). The flooring oils were applied according to the manufacturers' instructions for use on wooden flooring boards. The substrates were seasoned and conditioned oak, beech and ash wood flooring boards of radial and semi-radial texture, with dimensions of 1000x120x21mm in the longitudinal, radial and tangential orientations respectively. The oxidative oil was applied on the wood samples in the laboratory for wood in construction of the Faculty of Forestry (LDG) under standard laboratory climatic conditions (23±2°C i 50±5% rel. humidity).

Dry film thickness measurement was carried out according to standard HRN EN 13696:2010 with a resolution of ±2 μm. The procedure is based on the use of an optical light microscope with 100 to 200 times magnification, equipped with a camera and appropriate image analysis software. Scratch resistance was measured as defined by HRN EN 438-2:2008 using scratch tester with a rotary table. Evaluation of results was carried out as defined by HRN EN 438-2:2008. Slip resistance was tested as defined in HRS CEN/TS 15676:2010 using a pendulum test in dry conditions. Resistance to chemical agents was tested according to HRN EN 13442:2013 using distilled water, detergent, ethanol, red wine, olive oil, blue ink, cow's milk, coffee, black tea, ammonia and acetone. All the surfaces tested were graded from 5 (no changes) to 1 (most severe changes) and the results were later expressed as the average of all individual values.

RESULTS AND DISCUSSION

Three main variables were tested during this experiment - scratch resistance, slip resistance and resistance to chemicals - and the results correlated with the film thickness of wood protected with UV varnish (UVL), UV oil (UVO) and oxidative oil (O). It should be pointed out that the range in film thickness (Figure 1) with all the variables tested was narrow (50 to 70 μm on UV varnished surfaces and 18 to 22 μm on surfaces protected with oxidative oil and UV oil) which enables the influence of this factor on the variables tested to be eliminated.

The surfaces of all the unfinished substrates, unmodified and thermally modified, as well as those protected only with oxidative oil exhibited very poor scratch resistance, indicating that the oxidative oil cannot adequately protect surfaces from scratching. On the other hand, UV oil, and especially the UV varnish applied to all the wood species tested exhibited much better behaviour (Figure 2).

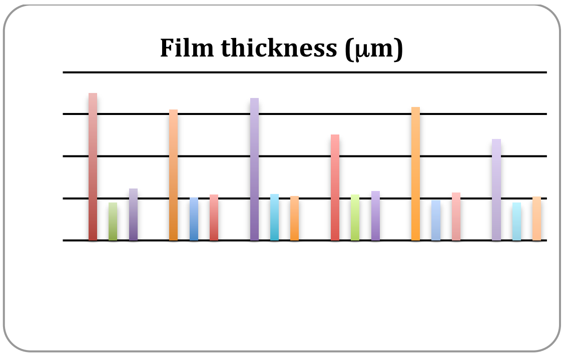

Figure 1: Film thickness of all tested variables in µm acc to EN 13696

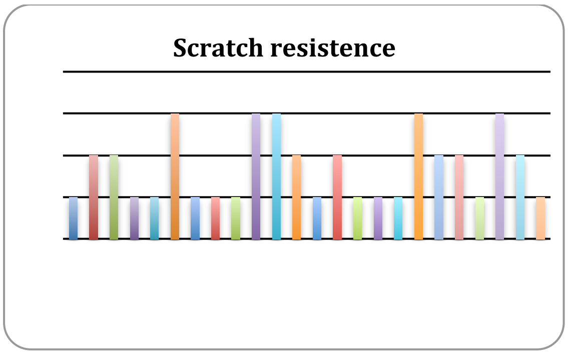

Figure 2: Scratch resistance of all tested variables acc to EN 438-2 (5 - best, 1 - worst)

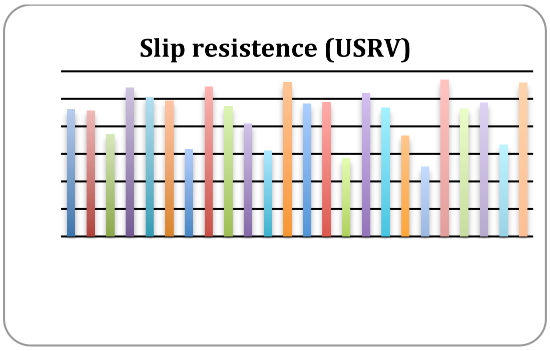

Figure 3: Slip resistance of all tested variables acc to CEN/TS 15676

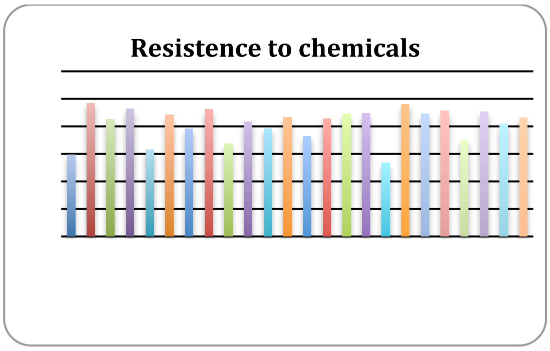

Figure 4: Resistance to chemicals acc to EN 13442

The slip resistance of all the variables tested was in the range from 55 to 110, which makes all these products safe for use, and only the UV oiled surfaces exhibited a slipperiness that was too excessive for applications in sports areas as defined by EN 14904. The surface protection system exhibited a much greater influence on slip resistance than wood species or thermal modification process. Wood species protected with oxidative oil showed the highest slip resistance values, whereas the UV oiled surfaces were always the least resistant. This is mainly due to the fact that no intermediate sanding was applied between the two layers of oxidative oil (Figure 3).

The resistance to chemical agents' tests showed that the same type of surface protection treatment exhibited the same behaviour on all tested substrates. The resistance of the surface protection treatments can be ranked as follows: UV varnish (best), oxidative oil, UV oil, unprotected surfaces (poorest). It should be pointed out that all the surface protected flooring elements exhibited good resistance to chemicals, whereas unprotected wood exhibited significantly lower values. Nevertheless, the changes were less apparent on the unprotected surfaces of thermally modified wood compared to unmodified material. This is due to the darker shades of modified wood which made all further marks due to chemical agents less visible.

CONCLUSIONS

All the results obtained here show that the surface protection treatment has a much greater influence on the behavior of wood floor covering than the wood species or the modification treatment. Generally, surfaces protected with UV curing varnish exhibit the best properties. Nevertheless, both UV curing oil and oxidative oil which form a thin protective layer of 18 to 22 µm, showed very good resistance to chemical agents and slip resistance. Despite the fact that UV oil and oxidative oil exhibited similar results on wood flooring elements, a question that remains is how to ensure the regular maintenance and repair of these products.

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Dimensional Changes of Three *Eucalyptus* Woods Subjected to Two-Step Impregnation-Heat Treatments

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Keywords: rosin, wood treatment, swelling, *Eucalyptus*

ABSTRACT

The aim of the present study was to evaluate changes in the dimensional stability of *Eucalyptus cloeziana*, *Eucalyptus grandis* and *Eucalyptus saligna* woods subjected to two-step modification involving impregnation and heat treatment. Fifteen samples of each species, measuring 15 x 15 x 15 mm were prepared. The first step of the combined treatments was the impregnation of wood with a rosin-based thermoplastic adhesive using two methods: vacuum impregnation-immersion (VT) and hyperbaric vacuum-pressure at 6000 bar (HBT). The second step of the combined treatments was heat treatment of the wood at 180°C for 30 minutes. All samples were oven-dried at 40°C and subsequently immersed in water for 24 hours. Volumetric (αv), radial (αr) and tangential (αt) swelling was determined. The best retention of solution was observed for *Eucalyptus grandis* wood (3.23%). As observed in the Rs parameter, the volumetric, radial and tangential swelling of woods was also higher after HBT treatment. This suggests that the wood cells break due to the high pressure applied, allowing the formation of linkages with water molecules. On the other hand, VT treatment did not significantly improve the dimensional stability of the woods, since the average values were similar to those found in untreated samples.

INTRODUCTION

Wood is an organic and renewable material which can be found in many applications. It can be found in buildings, pulp and paper, bioenergy, in the production of panels and in the furniture industry. Nevertheless, its intrinsic characteristics, such as hygroscopicity and susceptibility to biodeterioration limit the use of wood. Thus, alternatives to protect wood against these limitations are needed.

In the last few decades many techniques have been developed in order to improve wood's properties, particularly its resistance to biodeterioration. These include impregnation with CCA and CCB, in situ polymerization and thermal treatments (Mattos *et al.* 2015, Esteves *et al.* 2011, Hill 2006). Amongst these techniques, impregnation with biopreservatives and thermal treatments can be highlighted.

Wood impregnation with natural products is an important alternative to improve its properties and to support different applications in the market. Moreover, the use of natural products is important to satisfy demands for sustainable products.

Thermal treatment is a process involving exposing wood to high temperatures wherein degradation of its chemical components results in physical, mechanical and biological changes. An increase in dimensional stability and a decrease in the hygroscopicity of thermally treated wood can occur concurrently with weight loss along with a decrease in mechanical strength (Esteves *et al*. 2011, Rowell *et al*. 2013).

Scientific studies have been tried with the aim of developing two-step methods, to include both impregnation and thermal modification. For example, wood impregnation with borates followed by thermal modification (Awoyemi and Westermark, 2005) and melamine-urea impregnation followed by heat treatment (Lahtela and Kärki, 2014).

In this study, a thermoplastic adhesive containing rosin - a promising material extracted from pine resin - was used in wood impregnation. This byproduct of pine resin is an alternative to improve different characteristics, especially wood's hydrophobicity. The aim of this study was to evaluate the effects of two-step impregnation-heat treatments on the dimensional stability of *Eucalyptus cloeziana, Eucalyptus grandis* and *Eucalyptus saligna* woods.

EXPERIMENTAL

Eucalyptus cloeziana, *Eucalyptus grandis* and *Eucalyptus saligna* trees were cut from a homogeneous plantation located in the state of Rio Grande do Sul, Brazil. The first log of each tree was cut and wood samples having dimensions of 15 x 15 x 15 mm were prepared. All the wood samples prepared were kept in a climatic chamber (temperature 23ºC and 50% relative humidity) to reach equilibrium moisture content.

Two-step impregnation-heat treatments were performed. The first step was the impregnation of the wood with a rosin-based thermoplastic adhesive using two methods: vacuum system (VT) and hyperbaric pressure at 6000 bar (HBT). Thermoplastic adhesive was supplied by SONAE Industry (Aveiro, Portugal). The adhesive was diluted in toluene (concentration of 8.2% w/v).

In the VT method, a vacuum was applied for 15 minutes and then the preservative solution was introduced into the chamber. The wood impregnation was performed for 3 hours. In the HBT method, the wood samples were inserted in sealed flasks containing the preservative solution for 3 hours. These flasks were kept in a hyperbaric chamber and then were exposed to a pressure of 6000 bar for 15 minutes at room temperature (22ºC). After this stage, the wood samples were removed from the flasks and oven-dried at 40°C for 12 hours.

The second step was heat treatment in an oven with forced-air circulation. All the wood samples were exposed at 180°C for 30 minutes. After this step, the wood samples were kept in a climatic chamber to reach equilibrium moisture content.

The retention of the solution (Rs) and the weight loss (WL) of the treated wood samples were determined according to the UNE EN 351-1 (2010) standard and the method described by Cademartori et al. (2013), respectively.

Changes in the swelling of wood was measured after its immersion in water for 24 hours. The weight and dimensions (radial, tangential and longitudinal) of the wood samples were measured. Thus, volumetric (αv), radial (αr) and tangential (αt) swelling was determined according to Brazilian National Standard -NBR 7190 (ABNT, 1997).

RESULTS AND DISCUSSION

HBT treatments resulted in the highest levels of retention of solution and weight loss in the woods (Figure 1). According to Ribeiro (2011), hyperbaric treatment promotes the penetration of preservative into the wood micropores due to the high pressure applied.

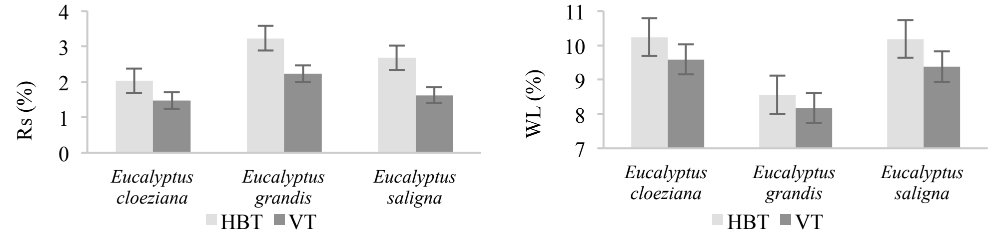

Figure 1: Average values of retention of solution (Rs) and weight loss (WL) of Eucalyptus woods. Error bars correspond to standard deviation

Among the eucalypt treated woods (VT and HBT), *Eucalyptus grandis* presented the best Rs results, followed by *Eucalyptus saligna* and *Eucalyptus cloeziana*. This suggests that the level of solution retention in each wood is influenced by the anatomical characteristics and density. The density of *Eucalyptus grandis* wood is lower than the density of *Eucalyptys saligna* and *Eucalyptus cloeziana* woods, which can ease the impregnation of liquids in the cell wall.

Regarding weight loss, HBT treatments were affected more by wood structure than VT treatments. This occurred due to a higher retention of solution (Rs) in wood treated with hyperbaric pressure. Heat treatment at 180°C tends to degrade the chemical structure of wood, especially hemicelluloses. Moreover, softening of rosin occurs at 77°C (Lopes 2011), which can contributes to the weight loss after heat treatment.

Eucalyptus cloeziana wood presented the highest swelling values in all the anatomical directions and type of treatments (control, VT and HBT). The average values of radial, tangential and volumetric swelling showed a slight decrease after VT treatments in comparison to the control treatment (Figure 2). On the other hand, HBT treatment resulted in an increase in swelling. Lesar et al. (2011) pointed out that OH bonds present in the wood structure and the interaction with water molecules significantly influences the efficiency of wood treatments in reducing hygroscopicity. Note that thermoplastic adhesives do not form bonds with OH groups available in the wood structure, allowing them to bond with water molecules.

This suggests wood cells break due to the high pressure applied in HBT treatments, which allows the formation of linkages with water molecules and, consequently, an increase in swelling. Thus, VT treatments were more effective in protecting wood than HBT treatments, blocking the absorption of water in wood voids.

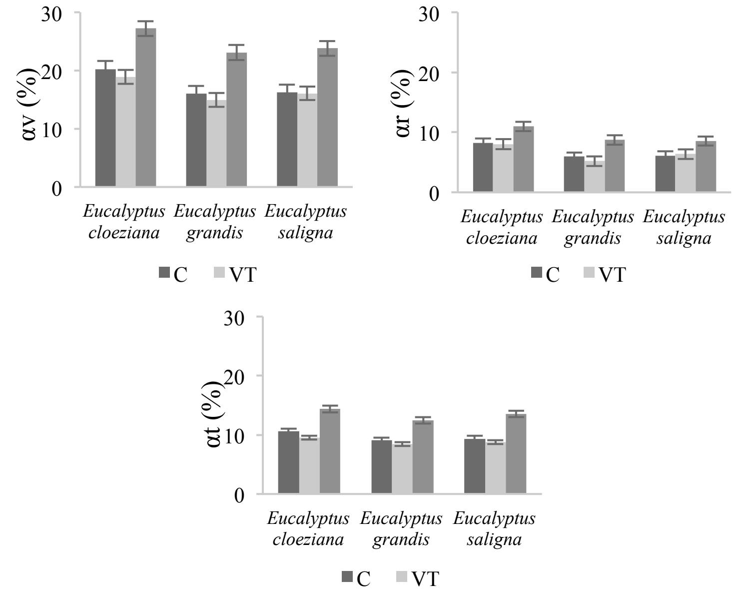

Figure 2: Average values of volumetric, radial and tangential swelling of Eucalyptus woods. Error bars correspond to standard deviation

CONCLUSIONS

- In general, two-step impregnation-heat treatments did not significantly improve the dimensional stability of *Eucalyptus* woods.
- In HBT treatments it was interesting to note the increase in the retention of solution. Nevertheless, the use of hyperbaric pressure may have affected the wood's anatomy, which influenced its dimensional stability.
- VT treatments resulted in a slight increase – especially for volumetric swelling – in the dimensional stability of *Eucalypts* wood. An increased impregnation time is recommended to improve the effect of the two-step treatments.

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Set-Recovery of Heat Treated Maritime Pine Wood Prior and after Compression

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Keywords: compression, heat treatment, *Pinus pinaster*, set-recovery

ABSTRACT

Pine (*Pinus pinaster*) wood samples were subjected to a combined densification and heat treatment process. Samples were densified before and after heat treatment. The heat treatment was carried out inside an oven at 190ºC for 2 to 6 h and wood densification was performed in a hot press at around 48 bar pressure and at temperatures of between 160ºC and 200ºC for 30 min. Compression rate and density were determined after the treatment. Set recovery was determined by thee cycles of water soaking followed by oven drying. The best results were attained when densification was done before heat treatment. The set recovery was less than 30% for the first two cycles and a little higher in the third cycle. For wood treated for 6 hours, the set recovery was less than 15%. Heat treatment before densification seems to be less effective than after densification to enable set-recovery.

INTRODUCTION

According to Morsing and Hoffmeyer (2000) the densification process can be divided into four steps, the first being softening or plasticization of the cell wall followed by compression perpendicular to the grain in the softened state, setting by cooling and drying in the deformed state and fixation of the deformed state. Springback when wood is re-moistened is one of the main problems with compressed wood. Morsing and Hoffmeyer, (2000) proposed three mechanisms to avoid springback, namely changing the hygroscopicity of the cell, forming covalent crosslinks between the wood components or releasing the elastic stresses and strains created during compression. Several authors have been testing the reduction in the hygroscopicity of the cell through heat treatment. For example Inoue *et al.* (1993, 2008) showed that it was possible to reduce springback by both dry heating and steam heating, although dry heating required 20 hours at 180°C to avoid recovery and 5-20 min are enough if steam heating is used. The intention of this work was to study differences between applying the heat treatment before or after compression.

EXPERIMENTAL

Pine wood (*Pinus pinaster*) from the Portuguese Viseu region was used in the tests. Sapwood samples with approximate dimensions of 145 mm x 145 mm x 32 mm (longitudinal x tangential x radial) were cut from a central board and placed in a controlled environment at 20ºC and 65% relative humidity for two weeks. The samples were subjected to a combined treatment by densification and heat treatment. Samples were densified before and after heat treatment in accordance with the parameters shown in ***Table 1*** and the compressive set after the treatments was determined. The heat treatment was carried out inside an oven at 190ºC for 2 to 6 h and wood densification was performed in a hot press at around 48 bar pressure and temperatures between 160ºC and 200ºC for 30 min. In order to determine the compressive set recovery, treated woods were subjected to three water soaking cycles followed by oven drying.

Table 1: Treatments

Sample	First treatment	Second Treatment
D160	Densification at 160ºC, 180ºC or 200ºC	No treatment
D180		
D200		
DT1902	Densification at 160ºC, 180ºC or 200ºC	Heat treatment at 190ºC for 2h, 4h and 6h
DT1904		
DT1906		
T1902	Heat treatment at 190ºC for 2h, 4h and 6h	No treatment
T1904		
T1906		
TD1902	Heat treatment	Densification at 160ºC, 180ºC or 200ºC
TD1904		
TD1906		

RESULTS AND DISCUSSION

The compression set of untreated wood densified at 160-200ºC ranged from 45.4% to 46.9%. Although compression set increases with the pressing temperature the differences were not significant (Table 2). In relation to samples that were heat treated before compression, the compression set was around 13%. This means that to attain a similar compression in samples heat treated prior to compression, a higher pressing pressure would be necessary. Although the decrease in the dimensions of samples that were only heat treated are presented here as compressive set, no compression was carried out. The decrease in the dimensions is only due to heat treatment.

The final density was around 1040 kg/m^3 for densified wood corresponding to a 70% increase in relation to untreated wood. The density of samples that were heat treated after compression decreased with heat treatment, reaching a final density of around 980 kg/m^3, representing a 62% increase in relation to untreated wood. For samples that were heat treated prior to compression, the maximum density obtained was around 630 kg/m^3 which mean that the final density represents just a 3% increase in relation to the initial state of the wood. The density of the samples that were only heat treated decreased by about 6% (Table 2).

Table 2: Compression set and final density

Sample	Compression set (%)	Final Density (kg/m^3)
D160	45.4	1048
D180	45.9	1031
D200	46.9	1041
DT1902	46.5	988
DT1904	45.7	973
DT1906	46.3	1002
T1902	2.2	577
T1904	2.4	569
T1906	2.8	562
TD1902	12.7	627
TD1904	12.8	633
TD1906	13.0	619
Untreated		531

Figure 1 presents the water soaking followed by oven drying cycles for treated and untreated samples. These tests showed that the set recovery of densified wood without heat treatment was around 80%, regardless of the pressing temperature. Almost all of the set recovery was obtained after the first wetting cycle. Even though after the third cycle the set recovery is slightly higher, the samples have a lot of checks due to the wetting/drying cycles which increases the radial dimension. The set recovery of heat treated wood before densification depends on the time of treatment. With a higher treatment time the set recovery is smaller. After the second cycle the recovery was about 70% for wood treated at 190 ºC for 2h whilst for 4h treatment the recovery reduced to 57% and for 6h to about 50%. In the third cycle the set recovery increased for all the treatments although there was already some damage in the samples due to the wetting/drying cycles.

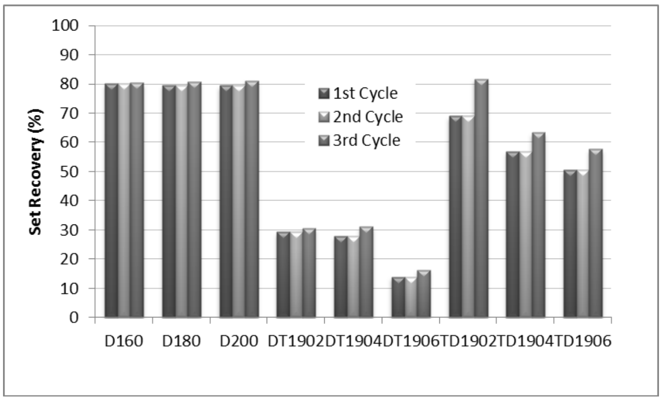

Figure 1: Set recovery after three wetting cycles

The best treatment was obtained when densification was followed by heat treatment. The set recovery was less than 30% for the first two cycles and a little higher in the third cycle. For wood treated for 6 hours, the set recovery was less than 15%. Heat treatment before densification seems to be less effective than after densification in reducing set-recovery. Nevertheless we have to take into account that the compression rate for heat treated wood is smaller. Tests are underway to try to obtain a similar compression rate on heat treated wood.

CONCLUSIONS

In conclusion to achieve the best results, densification must be done before heat treatment. The set recovery was less than 30% for the first two cycles and a little higher in the third cycle. For wood treated for 6 hours the set recovery was less than 15%. Heat treatment before densification seems to be less effective than after densification to reduce set-recovery.

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Effects of Thermal Modification on the Properties of Melamine-Impregnated Scots Pine (*Pinus sylvetris*) Wood

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Keywords: impregnation, melamine, heat treatment, properties, Scots pine

ABSTRACT

Wood, as a natural material, is a popular product in many applications. However, it has some weaknesses which can be improved by wood modification. The thermal modification of wood is a known method to improve the properties of wood without imposing undue strain on the environment. On the other hand, some mechanical properties may be impaired, whereupon the development of the heat treatment process is essential. This study investigates the improvement in the properties of melamine-impregnated and heat-treated solid wood. Scots pine (*Pinus sylvetris*) wood was modified in two stages: impregnation with melamine followed by heat treatment at temperatures of 180 °C and 212 °C for three hours. The properties of the modified samples were determined by physical and mechanical tests, which included, inter alia: water absorption, swelling, weathering, and strength tests. The results indicate a significant improvement of the properties investigated, particularly with regard to mechanical strength, the result of which was a positive surprise. It is concluded that some properties of melamine-impregnated wood can be enhanced by the thermal modification of wood, but the type of treatment parameters affect the results.

INTRODUCTION

Wood has a large number of applications, but some of its inherent properties, such as vulnerability to moisture and solar radiation, restricts its utilization. The modification of wood is an excellent way of improving its properties. Several methods of wood modification are known, such as chemical, thermal, or impregnation modification. However, combinations of these methods is not very common yet. Impregnation modification of wood creates the desired performance by filling the substrate of wood with an inert material (Hill 2006). Some properties of the modifiers, like pH, and a comparison between oil- and water-based ones, have an effect on the properties of wood (Nurmi *et al.* 2010, Simsek *et al.* 2010). Thermal modification of wood causes chemical changes by heating the wood at elevated temperatures and it is the most advanced modification process commercially (Hill 2006). However, the strength properties of thermally modified wood are reduced (Rowell *et al.* 2013). The aim of this paper is to briefly introduce the properties of melamine-impregnated and heat-treated wood that we have observed in previous work (Lahtela and Kärki 2014a, 2014b).

EXPERIMENTAL

Scots pine (*Pinus sylvetris* L.) was used in the investigation. The samples were treated by impregnation with melamine in a registered pressure apparatus, at a pressure of 10 bars for 120 min, after which the samples were dried in an oven at 90 °C for 24 h. The melamine solution (Prefere 70 0592 L) was supplied by Dynea Chemicals Oy. The heat treatment was performed in a heating oven, at temperatures of 180 °C and 212 °C for 180 min. The results of the impregnation and heat treatment were measured by weight percent gain (WPG) and mass loss (ML). Water absorption (WA) and swelling (S) were measured using 15 specimens with dimensions of 20 × 20 × 30 mm. The specimens were weighed and measured before and during immersion in water for a duration of 28 days. Weathering performance was determined by measuring the surface color with a Minolta CM-2500d spectrophotometer, according to the CIELAB color space. The specimens were passed through an accelerated weathering test for a duration of 1000 h. The test was based on intervals of UV-light and water spray according to SFS-EN ISO 4892-2. The strengths of 15 specimens were determined by three-point bending and impact strength tests in accordance with ISO 3133 and EN ISO 179. The size of the samples for bending strength were 20 × 20 × 380 mm and for impact strength 4 × 10 × 80 mm.

RESULTS AND DISCUSSION

The average WPG value of melamine was 38.71, and the average ML values were 8.14 and 11.00 after heat treatment at 180 °C and 212 °C temperatures respectively. The favorable WPG value of melamine may be due to its low viscosity (8–14 mPa·s) which has been found to affect the uptake of solution in pine wood (Tondi *et al.* 2013).

Water absorption and swelling

The water absorption and swelling properties are presented in Figure 1. The WA results are shown as a point chart with a two-period moving average trend line, and the S results are shown as a bar chart for the tangential and radial directions. The melamine-impregnated and heat-treated samples absorbed the least water throughout the test. In addition, the water absorption was reduced by the impact of the higher treatment temperature. The higher treatment temperature also reduced swelling. The melamine-impregnated samples had smaller swelling compared to the reference samples, especially in the tangential direction.

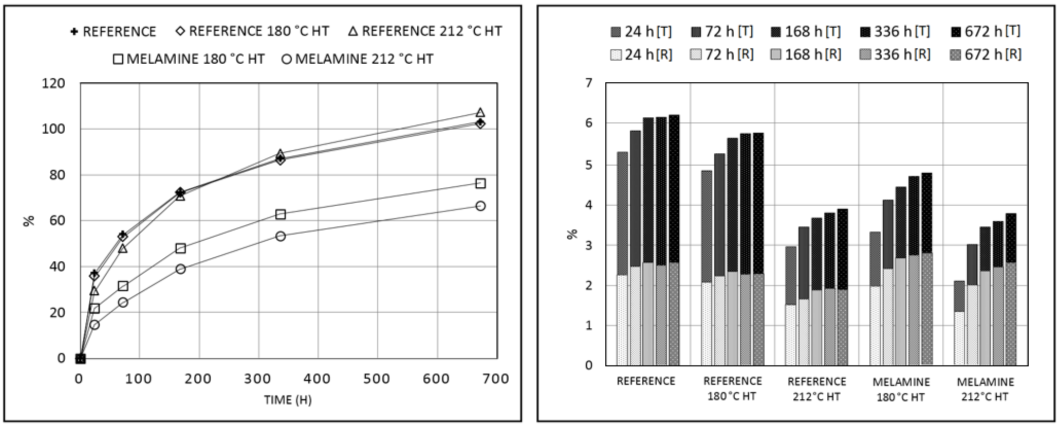

Figure 1: Water absorption as a function of immersion time (left), and tangential and radial swelling with time (right) (HT=heat treated, T=tangential, R=radial)

The benefit of melamine could be detected in the swelling test. The swelling of the melamine-impregnated samples increased regularly during the test while the swelling of the reference samples reached the maximum swelling values with dispatch.

Weathering

Weathering performance is represented in Table 1 by color difference (ΔE^*). The color change of the reference and melamine samples stabilized within 300 h, but the heat treatment had a significant effect on the color change of the melamine-impregnated samples. The ability of melamine to retain the natural appearance of wood has been presented previously by Hansmann *et al.* (2006). The melamine-impregnated and heat-treated samples at 180 °C temperature had the lowest color change at the beginning of the test, while the higher treatment temperature (212 °C) caused the largest color change with high standard deviations. The melamine-impregnated and heat-treated samples included tangential and radial surfaces. The tangential color change was bigger compared to the radial surface and it was highlighted with the greater heat treatment temperature, which is in agreement with a previous study of heat treated wood, depending on wood species (Huang *et al.* 2012).

Table 1: The total color change (ΔE^*)

Sample	100 h	200 h	300 h	600 h	1000 h
Reference*	9.47 (2.48)	11.14 (1.84)	10.95 (3.54)	-	-
Melamine*	9.73 (3.08)	8.99 (1.99)	8.23 (1.38)	-	-
Melamine 180 °C HT**	2.39 (0.89)	3.58 (2.16)	6.29 (3.35)	15.66 (3.67)	22.47 (2.39)
Melamine 212 °C HT**	13.79 (7.29)	19.96 (9.92)	23.76 (9.59)	32.11 (6.63)	37.99 (4.69)

*Values in parentheses indicate standard deviations (*average of 30 measurements, **average of 18 measurements)*

Strength

The strength properties are presented in Figure 2 as bar charts with standard deviations as error bars. In addition, polynomial trend lines have been added to Figure 2 as an emphasizing factor. The reduction in bending strength due to heat treatment became greater with increasing treatment temperature, in agreement with a previous study (Kocaefe *et al.* 2010), but with melamine impregnation strength was improved. The melamine-impregnated samples heat-treated at 180 °C and 212 °C had 10.0% and 21.7% better bending strength compared to the reference heat-treated samples respectively.

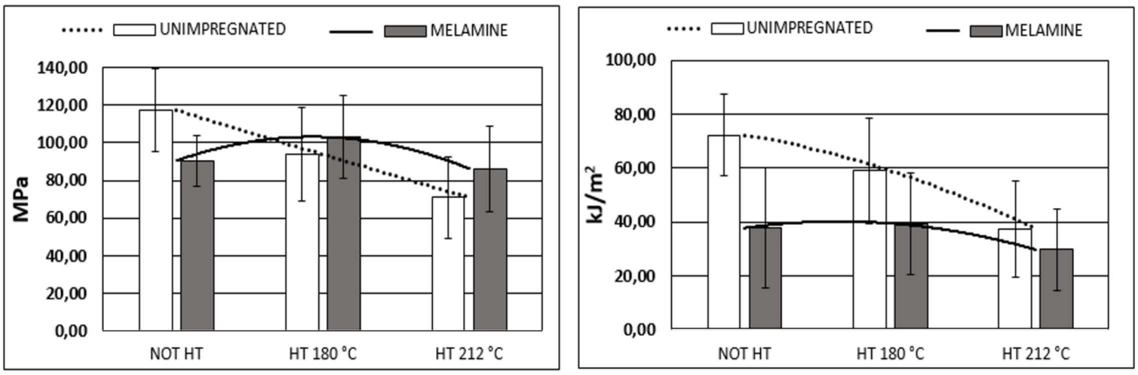

Figure 2: Bending strength (left) and impact strength (right) (HT=heat treated)

Impregnation and heat treatment impaired the impact strength. However, the impact strength of the melamine-impregnated sample, heat-treated at the lower temperature, remained at the same level as the impact strength of the melamine-impregnated samples without thermal modification.

CONCLUSIONS

The influence of heat treatment on the properties of melamine-impregnated wood were investigated in this study. Some conclusions can be drawn from the results. The weathering performance of thermally modified and melamine-impregnated wood depends on the treatment temperature. The water absorption test showed a lower uptake for melamine-impregnated samples, and a high heat temperature restrained the swelling of samples. The melamine impregnation of heat-treated wood resulted in an improvement in strength. Based on these preliminary findings, moderate thermal modification of melamine-impregnated wood seems to have a favorable impact on the properties of wood. Further studies are necessary to obtain more information on the features and to analyze the specific values for a profitable process.

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Thermal Modification of *Eucalyptus nitens*

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Keywords: colour change, dimensional stability, *eucalyptus nitens*, thermal modification

ABSTRACT

Thermal modification has been used to improve the properties of New Zealand-grown *Eucalyptus nitens*. *E. nitens* has low dimensional stability, and is not widely used for appearance-grade sawn timber production. Four thermal modification schedules, ranging from 150-210°C, were trialled in a laboratory-scale kiln and the properties of the modified wood measured, with a selection of these properties presented. All the schedules darkened the wood to a differing degree. The dimensional stability of the wood was improved in three of the four schedules, with ASE values of 60% for the wood modified at 210°C. Two schedules (185°C and 210°C) were chosen for further property testing; both schedules showed no reduction in MOE (stiffness), but had a 40-60% reduction in MOR (strength). Similarly, work to maximum load was reduced 70-80%, suggesting that the wood is much more brittle than it was prior to modification. Between-ring internal checks and ring-failure checks (cracks separating growth rings) increased with increasing thermal modification temperature. Between-ring checks tend to form late in the drying process, so it is possible that they are exacerbated by the early stages of thermal modification, where the wood is dried to a very low moisture content.

INTRODUCTION

Eucalyptus nitens (Deane et Maiden) Maiden is grown in the lower South Island and central North Island of New Zealand, and until now has been used for low-value applications such as pulp. Nitens is a pale-coloured wood, and is not especially dimensionally stable. These factors, along with difficulty drying the wood without degrade, are the main reasons that *E. nitens* is not more widely utilised as a sawn timber species. Thermal modification has been used successfully on many other species of eucalypt to alter the wood colour and improve dimensional stability (Esteves *et al*. 2008, Zanuncio *et al*. 2014), so it is hoped that thermal modification could be used to improve the properties of *E. nitens* to make it suitable for interior appearance applications. At Scion in Rotorua, four thermal modification schedules have been trialled on *E. nitens* boards, with the aim of enhancing the wood colour and improving dimensional stability, without causing excessive loss of strength and stiffness, or increasing drying degrade. A selection of the results to date is presented here.

EXPERIMENTAL

Four modification schedules were trialled in Scion's laboratory-scale thermal modification kiln. All schedules used the same heating and cooling phases, but each charge had a different high temperature phase, during which steam was added continuously to exclude oxygen from the kiln. The high temperature phases of the thermal modification schedules were chosen as follows: schedules similar to Thermo S and Thermo D for hardwoods (185°C, 197°C respectively, for two hours) as well as a schedule with a higher temperature than Thermo D (210°C for two hours) and one schedule with a temperature lower than Thermo S (150°C for six hours (Unsal *et al.* 2003)). The 150°C schedule did not require steam to exclude oxygen during the high temperature phase.

Thirty-nine 4-metre lengths of kiln dried *E. nitens* boards, 100x25mm in cross-section were obtained from a timber merchant in New Zealand's South Island. These boards were cut into five short (500mm) boards each to give five end matched charges of boards, for the four modification schedules, plus unmodified controls. After modification, the following property tests were performed:

Dimensional stability was measured using a water-soak/oven-dry test to calculate Anti-Shrink Efficiency (ASE). Biscuits were cut from boards from each charge, and their dimensions measured in both an oven-dried and water-saturated state. This was repeated for three water-soak/oven-dry cycles. ASE values were calculated from the second and third cycles. Further details of the method used can be found in Sargent *et al.* (2015).

Mechanical properties were evaluated via static 3-pt bending tests on samples 20x20x300mm according to BS 373 (1957). Tests were performed on samples from three charges (control, 185°C, 210°C). Results are presented as Modulus of Elasticity (MOE, a measure of stiffness), Modulus of Rupture (MOR, a measure of strength) and Work to maximum load (the energy absorbed by the sample before it starts to break, an indication of brittleness).

Degrade caused by modification was measured by assessing the cut face of 25 boards from three charges (control, 185°C, 210°C) for inter-ring (between-ring) checking and ring failure (cracks separating growth rings), which are known to occur in the later stages of drying (Ward & Simpson 1991), so may be increased by thermal modification. Inter-ring checking was assessed as being 'acceptable' or 'unacceptable'. Ring failure checks were recorded as being present or absent. Within-ring checking, and collapse appear in the early stages of drying (Ward & Simpson 1991), so have not been covered here.

RESULTS AND DISCUSSION

All modifications darkened the wood, and many colleagues commented on the attractiveness of the modified samples. Colour analysis has been performed on the modified boards and will be presented at a later stage. For all results presented below, superscript letters indicate results that are not significantly different (95% confidence). A modification temperature of zero indicates the unmodified control samples.

The ASE values are shown in Figure 1. There is a general trend towards increasing ASE, although the 197°C modification has extremely high variability compared to the other samples. The three highest modification temperatures have significantly higher ASE values than the controls. For these samples the median ASE values vary from 40-60%. It is not known what caused the high variability in ASE values for the 197°C schedule – there was nothing unusual about this thermal modification run that might have affected the level of modification.

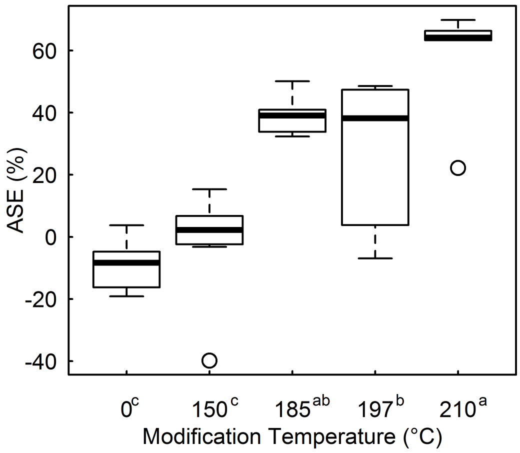

Figure 1: Anti-Shrink Efficiency (ASE) for each modification temperature.

Results from the mechanical property tests are shown in Table 1. MOE (stiffness) is unchanged by thermal modification. MOR (strength) is reduced by 40-60%, which is not necessarily of concern, but would need to be taken into account if the wood was to be used in load bearing applications (e.g. window joinery, flooring). Work to maximum load is substantially reduced with increasing modification temperature, suggesting increased brittleness in the modified wood. This would need to be investigated further, if desired applications required toughness.

Table 1: Average Mechanical Properties for each schedule

	MOE [GPa]		MOR [MPa]		Work [kJ/m^3]	
Schedule	**mean**	**% loss**	**mean**	**% loss**	**mean**	**% loss**
0	12.4^a	-	117.1^b	-	243.6^d	-
185	12.7^a	-2	73.2^c	38	75.6^e	69
210	11.2^a	10	48.7^c	58	50.9^e	79

Inter-ring checking and ring-failure checking were not visible in any of the control boards, but were visible in many boards after modification; moreover both had an increasing incidence with increasing modification temperature (Table 2).

Table 2: Proportion of boards with unacceptable levels of degrade

Schedule	Boards with unacceptable inter-ring checks (%)	Boards with ring failures (%)
0	0	0
185	48	28
210	68	40

These defects are known to be exacerbated by severe drying, so it is not surprising that the incidence of these might increase with increasing modification temperature, because the initial stages of thermal modification dry the wood to very low moisture contents.

CONCLUSIONS

From the results presented here, thermal modification appears to offer the means to improve the dimensional stability of *E. nitens*, as well as darkening the colour. The stiffness (MOE) of the modified wood is unchanged, but the strength (MOR) is significantly reduced, as is the work to maximum load, suggesting that the modified wood is substantially more brittle following modification. For applications where strength and toughness are a concern, further testing would be required. Further property testing of this wood (including colour measurement) is currently underway and will be presented separately. Increasing modification temperature may increase the incidence of inter-ring checks, and ring-failure checks.

ACKNOWLEDGEMENTS

Steve Riley, Keith Walker, Paul Smith and Richard Dandoroff made the modifications to our laboratory kiln that made this work possible. Steve in particular developed the schedules and control system modifications to allow us to do thermal modifications using a standard kiln, and standard DRYSPEC control software. John Fairweather at Specialty Timber Solutions sourced and dried the timber for us. Steve Chapman assisted with wood preparation. Gavin Durbin and Maxine Smith assisted with the property testing work.

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Development of a Method for the Surface Modification of Wood

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Keywords: hot-and-cold bath process, non-pressure method, surface modification of wood

ABSTRACT

This study concerns the development of a method for surface modification based on the hot-and-cold bath process. In the experiments wooden boards were first heated in an oven and after that they were immediately soaked in a cold chemical solution. This procedure allowed the chemicals to penetrate partially into the wood without using pressure equipment. In this study copper, furfuryl alcohol and phenol formaldehyde based solutions were used. The impregnation resulted in modified layers below the wood surfaces representing a trade-off between full-bulk modification and surface coating of wood. It is concluded that the method can be developed further for potential industrial use to produce e.g. flooring, cladding or decking.

INTRODUCTION

Wood surface modification is often understood as a superficial modification on top of wood surfaces or as coating. At Luleå University of Technology the aim of surface modification is not only to apply coatings, but also to make chemicals penetrate deeper and create a significant layer of chemicals below the surfaces without using any pressure equipment. Why is this method attractive? Because it proposes a trade-off between full-bulk modification and surface coatings. Surface coatings only provide a limited amount of protection in terms of service life, while full-bulk modification is limited due to the high added cost of chemicals and expensive pressure impregnation processes needed to make the chemicals penetrate through the entire volume.

The method studied is based on a process referred to by different authors as the hot-and-cold-bath process or treatment, the boiling-and-cooling method, and open-tank treatment or thermal process (Hunt and Garratt 1967, Kollmann and Côté 1984, Ormrod and Van Dalfsen 1993). In this method, the wood is first heated and directly after heating the material is submerged into a cold preservative solution (Hunt and Garratt 1967, Kollmann and Côté 1984). The heating can be done in preservative, water or in a drying kiln and this makes the air in the outer layers of the wood expand (Hunt and Garratt 1967, Kollmann and Côté 1984). Immediately after heating the material is immersed into the cold solution wherein the air in the material contracts. The contraction of the gases inside the wood should create the equivalent of localized vacuum suction under the wood surfaces; and this helps to push the preservative into the wood (Hunt and Garratt 1967, Kollmann and Côté 1984). The efficacy of such a method will depend, among other factors, on the size of the molecules and the viscosity of the impregnation solution, as well as the temperature difference and the treatment exposure time.

In earlier studies, the method was applied using water-soluble salts, coal-tar creosote and other preservative oils (Hunt and Garratt 1967, Kollmann and Côté 1984). At Luleå University of Technology this method was applied with vegetable oils (Sidorova 2008, Sidorova and Morén 2010, Karlsson *et al.* 2011, Ahmed and Morén 2012, Ahmed *et al.* 2013a-b). However, it was mainly used for wood impregnation without considering the direction of the wood fibres. Since permeability in the radial and tangential directions of the wood is much lower than in the longitudinal direction, the question is whether the method could be applied to penetrate only the board faces which could be used for e.g. decking, flooring or panelling.

EXPERIMENTAL

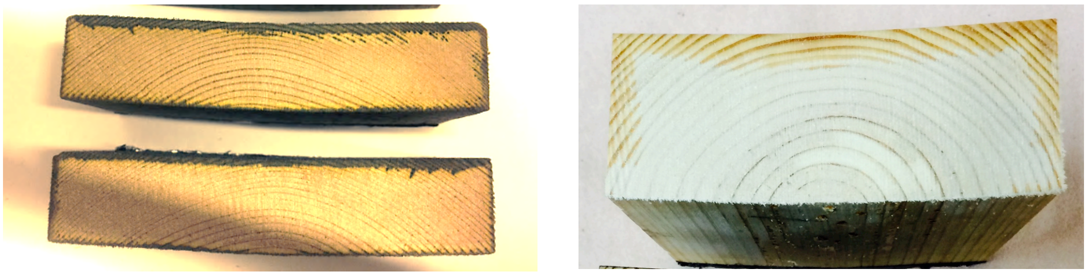
The samples were kiln dried flat sawn boards of Scots pine (*Pinus sylvestris* L.) from Northern Sweden with dimensions of approximately 95 x 120 x 20 mm (L x W x T). The cross-sections of the samples were sealed with silicone glue to avoid penetration of the chemicals through the end surfaces, thus only penetration through the radial and tangential sections was analysed. Prior to the treatment the samples were dried at 103°C for 12 hours.

The method was implemented as follows: The samples were heated in an oven for 2 hours at a temperature of 130°C and then soaked whilst they were still hot in a chemical solution that was initially at room temperature. The samples were maintained in the cold solution for 30 minutes while they cooled down and absorbed part of the chemicals through the surfaces. The chemical solutions tested were a copper solution, vegetable oil, furfuryl alcohol, and phenol formaldehyde resin. As an example, Fig. 1 shows samples submerged in cold phenol formaldehyde resin. It can be observed that both samples and resin were placed in aluminium containers, and the samples were held by loads to guarantee full immersion. The aluminium containers were partially submerged in a mixture of water and ice to maintain the impregnation solution at a temperature of approximately 5°C.

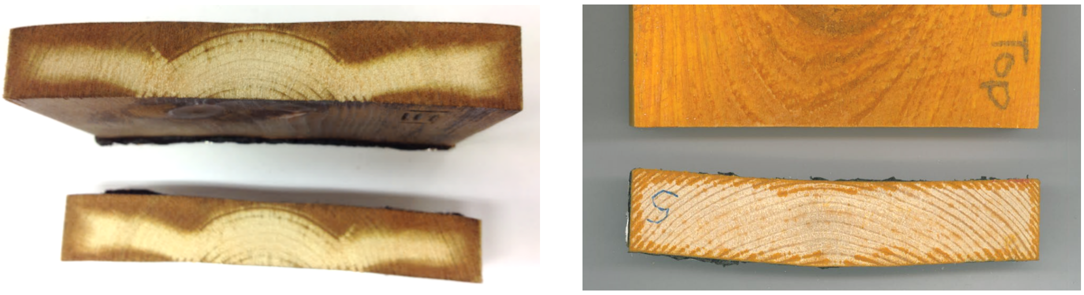
Figure 1: Samples submerged in cold liquid solutions and pressed by loads

RESULTS AND DISCUSSION

The method was tested with several impregnation solutions based on the fact that they change the colour of the impregnated wood. In all cases, the results showed a noteworthy impregnation of the wood closest to the surfaces, but there were different levels of penetration depending on the solutions used. The results showed that penetration can go from a couple of millimetres in the case of the copper solution to almost one centimetre in the case of furfuryl alcohol (Fig. 2). It was concluded that depending on the case, the proposed method might provide an intermediate solution between simple dipping and batch pressure treatment.



Copper solution Vegetable oil



Furfuryl alcohol Phenol formadehyde resin

Figure 2: Examples of exploratory tests of localized surface modification

In the cases studied, the viscosity of the solution had a much greater effect on penetration than the temperature of the treatment. It was also noticed that even though the penetration was not as deep as in pressure treatment, the method studied facilitated impregnation through the resin canals.

CONCLUSIONS

This study presents a new way of using the hot-and-cold bath method to modify a certain thickness of material under the wood surfaces. In other words, this study showed that the hot-and-cold bath method can be used as a trade-off between full-bulk modification and surface coatings, at least for the chemical solutions tested. This study proved that the method works in the laboratory, but the economic viability still needs to be proven before moving to industrial implementation. The next step of this study therefore will be to investigate if the proposed surface impregnation can be performed fast enough and if the resulting modified layer below the wood surface is uniform and thick enough to significantly increase durability and reduce the maintenance of solid wood.

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Preliminary Evaluation of the Thermomechanical Treatment of Tropical Hardwood Lumber

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Keywords: densification, flooring, tropical hardwood

ABSTRACT

Tropical woods used for flooring usually have high density which means high values of strength and stiffness. They also have good natural durability, but sometimes dimensional stability is a concern. Thus, thermal treatments can be useful for improving the dimensional stability. In this context, the aim of this study was to evaluate the properties of four tropical woods thermomechanically treated for the production of hardwood flooring. Four wood species from well-managed and legally established exploratory forest areas were evaluated: cedrinho (*Erisma uncinatum*), angelim (*Hymenolobium*), tachi preto (*Tachigali myrmecophila*) and mandioqueira (*Qualea paraensis*). For each species, six wood planks were cut to dimensions of 100 mm x 300 mm (W x L) with thicknesses ranging from 20 mm to 25 mm. From each plank one squared sample (30 mm x 30 mm) was obtained. The thermomechanical treatment was performed using a simple-opening hot press, under following conditions: 145ºC, from 21 to 30 minutes at pressures ranging from 1.4 to 3.6 MPa. The results showed that thermomechanical treatment significantly increased density only in angelim and mandioqueira, since these species presented the highest values of compaction ratio. The others species were not significantly densified. For all species, thermomechanical treatment ensured good dimensional stability. The wettability of the woods was reduced. Except for cedrinho, all species had an improvement in mechanical properties after the thermomechanical treatment. Although it was a preliminary study about the thermomechanical treatment of some Brazilian tropical hardwoods, good results were obtained. This should encourage further research in the field to evaluate other temperatures, durations, pressures and species.

INTRODUCTION

The modification of wood properties using thermal, chemical or mechanical processes has been extensively studied throughout time (Arruda and Del Menezzi 2013). However, in recent years research efforts have focused on thermal modification combined with mechanical compression, which is known as thermomechanical modification. In these processes the wood is thermally treated and at same time is compressed, leading to a density improvement. The main advantage is to minimize the usual drawback of thermal modification: the huge reduction in mechanical properties. As the wood is densified, the mechanical properties usually do not reduce. On the other hand wood treated this way incorporates high levels of compressive stresses which can be released when it is in contact with water, significantly increasing the thickness swelling.

Wood species used for flooring manufacture usually have high density, high mechanical properties and high natural durability, but the dimensional instability can be an important issue. Nowadays, the utilization of tropical hardwoods for flooring manufacture in Brazil is concentrated on 12 to 14 species. In this way, it is important to bring new species to the market and reduce the harvesting pressure on those species. In this case, one proposal is try to introduce wood species whose density is not high enough to be used as flooring. Sometimes, this material also does not have the required natural durability and dimensional stability. Therefore, the thermomechanical modification of this material could be a useful way to improve the properties of those new wood species. In the last few years some research has been done with the objective of modifying low density hardwoods using thermal treatments (Del Menezzi *et al.* 2014, Costa and Del Menezzi 2014, Arruda and Del Menezzi 2013).

In this context, the aim of this study was to evaluate the properties of four tropical woods thermomechanically treated for the production of hardwood flooring. This research was developed under the auspicious of the International Tropical Timber Organization (ITTO) and the Brazilian Government that funded the project “Sustainable Model for the Brazilian Wood Flooring Production Chain-433/06 R3 (1)”.

EXPERIMENTAL

Four wood species from well-managed and legally established exploratory forest areas belonging to the Brazilian Government were evaluated: cedrinho (*Erisma uncinatum* Warm., ρ=680 kg/m^3), angelim (*Hymenolobium* sp. ρ=710 kg/m^3), tachi preto (*Tachigali myrmecophila* Ducke ρ=730 kg/m^3) and mandioqueira (*Qualea paraensis* Ducke ρ=810 kg/m^3). For each of the species, six wood planks were cut to dimensions of 100 mm x 300 mm (W x L) with thicknesses ranging from 20 mm to 25 mm. From each plank one squared sample (30 mm x 30 mm) was cut and used to measure physical properties before the thermal treatment.

The thermomechanical treatment was performed using a simple-opening hot press. Pre-tests using a range of temperature revealed that 145ºC presented the best behaviour. Thus, the thermomechanical treatment was applied at this temperature and the pressure was that equal to 25% of the perpendicular compression strength of the respective species being treated: values ranged from 1.4 to 3.6 MPa. The internal temperature of the plank during the treatment was measured and when it reached the set temperature, 50% of the pressure was released. This condition was maintained for 5 minutes and then 100% of the pressure was released. In order to minimize the springback phenomenon, a post-treatment was applied and the planks were kept in the press (without pressure, only contact) for further 5 minutes. Thus, the treatments lasted between 21 and 30 minutes, depending on the wood species. Afterwards, the material was tested to assess the physical, mechanical and surface properties.

RESULTS AND DISCUSSION

The results showed that thermomechanical treatment significantly increased density only in angelim and mandioqueira, since these species presented the highest values of compaction ratio. The others species were not significantly densified. For all species, thermomechanical treatment ensured good dimensional stability, as demonstrated by the thickness swelling being lower than the compaction rate. This meant that the compressed form was retained in part after immersion in water. Another important factor was the reduction of EMC. Cedrinho had the most significant reduction, at 48.7%, followed by angelim with a 43.7% reduction. The colour of all species became darker, with predominantly reddish and brownish tones (Figure 1).

Figure 1: Color of the samples before and after treatment defined according color table from Camargos and Gonçalez (2001)

The wettability of the woods was reduced, represented by an increase in the water contact angle. With the exception of cedrinho, all species showed an improvement in mechanical properties (modulus of rupture, modulus of elasticity, Janka hardness and parallel compression strength) after thermomechanical treatment. The property that was the most positively affected by the treatment was modulus of elasticity, which had a maximum improvement of 65.2% for the angelim samples.

CONCLUSIONS

Although it was a preliminary study about the thermomechanical treatment of some Brazilian tropical hardwoods, good results were obtained. They should encourage further research in the field, trying to evaluate other temperatures, durations, pressures and species. Furthermore, for the material treated in this way, the machinability must be tested.

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Hot-Pressing Schedules for Thermomechanical Modification of Wood

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Keywords: densification, pine wood, springback

ABSTRACT

The utilization of compression combined with thermal treatment has been extensively studied. Nevertheless, wood treated in this way usually possesses a high level of compression stress and tends to return to its original shape. This phenomenon is known as shape memory or compression-set recovery. In this context, the main goal of this paper was study several strategies to overcome or minimize this problem and thus improve the dimensional stability of densified wood. Pine wood from plantation trees was used in this research. Approximately 72 samples measuring 10 mm x 100 mm x 20 mm (length x width x thickness) were obtained. The thermomechanical densification process was conducted using a single-opening hot-pressing and consisted of the following steps: heating-compression with pressure (HCP), heating without pressure (WPS) and thermal post-treatment (PT) applied at the end of the process. WPS and PT were considered strategies to reduce the compression-set recovery of the treated wood. Six different hot-pressing schedules based on temperature (160ºC/190º), time without pressure during the heating stage (WPS; 0′/10′) and the time of thermal post-treatment (PT; 0′/10′) were evaluated. Compaction rate (CR), mass loss (ML), equilibrium moisture content (EMC), thickness swelling (TS) and water absorption (WA) were determined. The results showed that utilization of the higher temperature (190ºC) has a significant effect on the improvement in dimensional stability and density. All wood-water related properties were consistently better in comparison with those obtained from wood treated at lower temperature (160ºC). It was also found that samples treated at 160ºC benefited more when further thermal post-treatment (PT) was applied. On the other hand, when the samples were treated at 190ºC, the release from pressing for 10 minutes (WPS) was more effective in reducing compression-set recovery. Thus, it could be concluded that the best schedule found was heating/compressing the sample for 20 minutes, followed by 10 minutes without pressure neither further post-treatment because it imparted better dimensional stability and higher compaction ratio.

INTRODUCTION

The modification of wood properties using thermal, chemical or mechanical processes has been extensively studied throughout time (Arruda and Del Menezzi 2013). The objective is an improvement in properties, mainly natural durability and dimensional stability. However, these processes often cause wood mass loss, which imparts a reduction in the mechanical properties. The use of compression combined with thermal treatment has been a natural approach to minimize such adverse effects. As such, wood is heated and compressed at the same time, which promotes its densification and thus reduces the negative effects on mechanical properties (Vasconcelos and Del Menezzi 2013).

Nevertheless, wood treated in this way always possesses a large amount of latent compression stresses, which can be released when the wood is in contact with water. This phenomenon is known as shape memory or compression-set recovery, whose origin is in the wood cell-wall ultrastructure and molecular structure. As these stresses are released, the wood dimensions vary substantially and the desired dimensional stability cannot be achieved. Pressure was the other variable studied by the authors to evaluate the thermomechanical treatment effect. Pressure increase is related to compaction ratio increase, which is directly related to densification (Bekhta *et al.* 2012). In this context, the main goal of this paper was study several strategies applied during the densification process to overcome or minimize this problem and thus improve the dimensional stability of the densified wood.

EXPERIMENTAL

Wood material and thermal treatments

Pine wood (*Pinus* spp.; ρ=474 kg/m^3) from plantation trees was used in this research. Approximately 72 samples measuring 10 mm x 100 mm x 20 mm (length x width x thickness) were obtained. Initially the material was kept in an air conditioning room (20ºC/65% RH) to reach constant mass. Afterwards, the boards were randomly separated into six groups in which the density of the samples ranged from 469 to 479 kg/m^3. Tukey test at α=0.05 revealed that the mean densities of the six groups were statistically equal.

The thermomechanical densification process was conducted using a single-opening hot-press (INDUMEC, 1000 kN) with the automatic control of temperature and pressure, and consisted of the following steps: heating-compression with pressure (HCP), heating without pressure (WPS) and thermal post-treatment (PT) applied at the end of the process. The pressure applied was about 2.5 MPa (≅ 50% of the perpendicular compression strength) and was kept constant during the HCP step due the automatic adjustment of pressure. During the WPS step, the sample was kept in the hot-press but the pressure was fully released. PT was applied one week later and consisted of simply heating the boards using the hot-press without any pressure, as described by Del Menezzi et al. (2009). WPS and PT were considered strategies to reduce the springback of the treated wood.

Six different hot-pressing schedules based on temperature (160ºC/190º), time without pressure during the compression stage (0´/10´) and time of thermal post-treatment (0´/10´) were evaluated, as can be seen in Table 1.

Table 1: Hot-pressing schedules evaluated in this study

Schedule	Temp [ºC]	HCP^a [min]	WPS^b [min]	PT^c [min]
S1	160	20	0	0
S2	160	20	10	0
S3	160	20	0	10
S4	190	20	0	0
S5	190	20	10	0
S6	190	20	0	10

^{a}*Heating-compression with pressure;* ^{b}*Heating without pressure;* ^{c}*Post-treatment.*

Afterwards, the samples were returned to the air-conditioning room (20ºC; 65%RH) and left to reach constant mass. Compaction rate (CR), mass loss (ML), equilibrium moisture content (EMC), thickness swelling (TS) and water absorption (WA) after 2, 24 and 48 hours of water immersion were determined.

Statistical analysis

Initially the results were analysed by running a simple analysis of variance (ANOVA), followed by Tukey's test, α=0.05, to compare the means values between six schedules. The isolated effect of temperature (160ºC *vs.* 190ºC) was evaluated by a simple F-test. The same procedure was used to evaluate the effect of time without pressure (WPS=S1 *vs.* S2, S4 *vs.* S5), post-treatment (PT=S1 *vs.* S3, S4 *vs.* S6) and to compare strategies (WPS/PT= S2 *vs.* S3, S5 *vs.* S6).

RESULTS AND DISCUSSION

During the heating-compression (HCP) step the hot-press was set to keep the pressure constant. Nevertheless, when wood is heated lignin loses stiffness, and passes from a glassy to a rubbery state. In this way, the pressure required to keep the wood deformation goes down (relaxation phenomenon) and thus the hot-press automatically adjusted to the pressure set and further wood densification occurred. The HCP step lasted 20 minutes and during this time between 8 to 11 pressure adjustments were made. The first adjustment usually happened when the sample reached between 32.9ºC and 59ºC whilst the last one was between 101.8ºC and 162.5ºC.

Table 2 shows the results according to temperature used. It can be seen that the utilization of the higher temperature (190ºC) has a significant effect on dimensional stability improvement and density (731 kg/m^3 *vs.* 797 kg/m^3). As can be observed all wood-water related properties were consistently better in comparison with those obtained from wood treated at lower temperature (160ºC).

Table 2: Isolated effect of temperature on properties of treated material

				WA [%]			TS [%]		
Temperature [ºC]	**EMC [%]**[a]	**ML [%]**	**CR [%]**	**2h**	**24h**	**48h**	**2h**	**24h**	**48h**
160	8.52	11.0	44.1	75.8	89.3	95.6	44.2	48.2	49.5
190	7.65	12.1	47.9	55.1	72.1	77.1	36.3	42.9	44.1

[a] *EMC: equilibrium moisture content; ML: mass loss; CR: compaction ratio; WA: water absorption; TS: thickness swelling.*

Table 3 shows all the results obtained according to the schedule tested. Taking into account all results, the EMC was about 8.1%, ML was 11.5%, while CR was 46%. The initial moisture content of the sample was about 11%, which means that the schedules used might promoted the drying of the sample and some very slight wood polymer degradation. However, it was enough to reduce the EMC of the treated sample from 11% to 8.1%.

Because of the temperature and the duration of the treatment, it can be inferred that the ML observed was due to the degradation of the hemicelluloses, the least thermally stable wood polymer. The mean compaction ratio (CR) was about 46%, which is close to the pressure used during HCP step: equivalent to 50% of the perpendicular compression strength of the wood.

Table 3: Properties of the treated material according to the schedule used.

Property	Schedule					
	S1	**S2**	**S3**	**S4**	**S5**	**S6**
ρ [kg/m^3]	737ab	746ab	712a	804b	802b	755a
EMC [%]	8.6b	8.5b	8.4b	7.8b	7.4a	7.7ab
ML [%]	10.9a	11.2a	10.9a	10.9a	12.6b	12.9b
CR [%]	45.1b	45.4b	41.8a	41.3a	50.6c	50.7c
WA2h [%]	79.1c	69.4bc	78.5c	61.4ab	46.3a	55.7ab
WA24h [%]	89.9bc	84.6bc	93.3c	75.5ab	65.9a	74.7ab
WA48h [%]	96.3bc	90.8bc	99.6c	80.3ab	71.2a	79.9ab
TS2h [%]	47.0c	43.7bc	42. bc	42.4bc	30.3a	37.0b
TS24h [%]	51.4c	48.4bc	45.7b	46.7b	37.1a	44.5b
TS48h [%]	52.1c	50.2bc	46.4b	47.7bc	38.8a	45.5b

[a] *Different letter on the same line means that the values are statistically different at α=0.05 according to the Tukey's HSD test.*

Tables 4 and 5 show the isolated effects of WPS, PT and the comparison between WPS x PT, for material treated at 160ºC and 190ºC, respectively. When the samples were treated at 160ºC, the release of the press after the HCP step affected only two variables: increased ML and reduced TS24H. On the other hand, the use of a 10-minute post-treatment improved dimensional stability (i.e. reduced TS and EMC), probably because it imparted lower CR. The post-treatment used here was similar to that used by Del Menezzi and Tomaselli (2006) and Del Menezzi *et al.* (2009), where the sample is reheated using the hot-press but without pressing. It is believed that the compression stress imposed during hot-pressing is released during this procedure, leading to lower values of thickness swelling when the sample is in contact with water. Post-treatment might be a better strategy than WPS when the samples are treated at 160ºC, since the EMC and TS48h showed lower values. In this situation the post-treatment might act as a further thermal treatment, imparting more mass loss and reducing adsorbed water.

Table 4: Effect of stage without pressure (WPS), post-treatment (PT) and comparison between WPS and PT for properties of material treated at 160ºC

Property	WPS Effect T1 (0) x T2 (10)	PT effect T1 (0) x T3 (10)	WPS x PT T2 (10) x T3 (10)
ρ [kg/m^3]	NS	NS	746 x 712*
EMC [%]	NS	8.65 x 8.39**	8.52 x 8.39*
ML [%]	10.9 x 11.2*	NS	NS
CR [%]	NS	45.1 x 41.8**	45.4 x 41.8**
WA2h [%]	NS	NS	NS
WA24h [%]	NS	NS	NS
WA48h [%]	NS	NS	NS
TS2h [%]	NS	47.1 x 42.2*	NS
TS24h [%]	51.4 x 48.4*	51.4 x 45.6**	NS
TS48h [%]	NS	52.1 x 46.4**	50.2 x 46.4*

[*,**] *Difference statistically significant at α=0.05 and α=0.01, respectively; NS: non-significant.*

The results of the material treated at 190ºC are presented in Table 5. In contrast to the results presented in Table 4, at 190ºC the release of pressure (WPS) had a significant effect on all evaluated TS properties. 10-minutes without pressure significantly reduced the TS2h, TS24h, TS48h, WA2h and EMC. Additionally the compaction ratio was also improved. On the other hand, at 190ºC, the post-treatment had no effect on the dimensional stability properties. A comparison between strategies shows that WPS was more effective than PT when the material is treated at 190ºC.

Table 5: Effect of stage without pressure (WPS), post-treatment (PT) and comparison between WPS and PT for properties of material treated at 190ºC

	WPS Effect	**PT effect**	**WPS x PT**
Property	**T4 (0) x T5 (10)**	**T4 (0) x T6 (10)**	**T5 (10) x T6 (10)**
ρ [kg/m^3]	NS	804 x 755**	802 x 755**
EMC [%]	7.85 x 7.43*	NS	NS
ML [%]	11.1 x 12.6**	NS	NS
CR [%]	41.3 x 50.6**	41.3 x 50.8**	NS
WA2h [%]	61.4 x 46.4**	NS	NS
WA24h [%]	NS	NS	NS
WA48h [%]	NS	NS	NS
TS2h [%]	42.4 x 30.3**	NS	30.3 x 36.9**
TS24h [%]	46.7 x 37.1**	NS	37.1 x 44.6**
TS48h [%]	47.7 x 38.8**	NS	38.8 x 45.5**

*,***Difference statistically significant at $\alpha=0.05$ and $\alpha=0.01$, respectively; NS: non-significant.*

CONCLUSIONS

Samples from pine wood were modified using six different hot-press schedules at two temperatures: 160ºC and 190ºC. It was found that the utilization of higher temperature led to better values of dimensional stability and compression ratio independent of the schedules used. Samples treated at 160ºC benefited more when further thermal post-treatment was applied. On the other hand, when the samples were treated at 190ºC releasing the pressure for 10 minutes was more effective in reducing the springback that usually happens in densified wood. Thus, it could be concluded that the best schedule found was heating/compressing the sample for 20 minutes, followed by 10 minutes without pressure neither further post-treatment because it imparted better dimensional stability and higher compaction ratio.

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Photostability of Thermally Modified Poplar Wood Superficially Treated with Some Protectants

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Keywords: photodegradation, poplar wood, UV protection

ABSTRACT

The purpose of the study was to determine the effectiveness of selected wood protectants against photodegradation. The study was performed on heat-treated poplar wood (*Populus* spp.) (Mazela 2010, Esteves 2009, Hill 2006). The following protecting agents were used for the wood surface treatment: UV filter (Tinuvin® 5050 - Tin), lignin stabilizer (Lignostab - Lign), nano-copper based colloidal solution (Nano-Cu) and a model preservative based on copper bicarbonate $Cu_2(OH)_2CO_3$ (model formulation - MF). The following acronyms were used respectively for the above mentioned protecting agents: Tin, Lign, Cu and ($Cu_2(OH)_2CO_3$). Tinuvin and Lignostab were used as penetrating or coating agents. The protected wood samples were submitted to an accelerated ageing procedure simulating natural weather conditions (ISO 11341-1). The colour changes were examined with the use of DataColor 600® system CIELab (Ayadi 2003, Lin 1970). No visible changes in the wood colour were observed after treatment with Nano-Cu. However, the ΔE value exceeded 6 after UV radiation. This means that Nano-Cu did not protect the wood surface against sunlight. Wood protective agents containing Tin or Lign caused clear colour changes in wood after treatment. Due to the ΔE value, which exceeded an index of 4 after UV radiation, their protecting properties were estimated to be insufficient as well. The best photo-stabilizing effect was demonstrated by a model preservative ($\Delta E < 2$) (Fig 1b). However, the impregnation process resulted in a visible change in the initial wood colour ($\Delta E > 7$) (Fig. 1a).

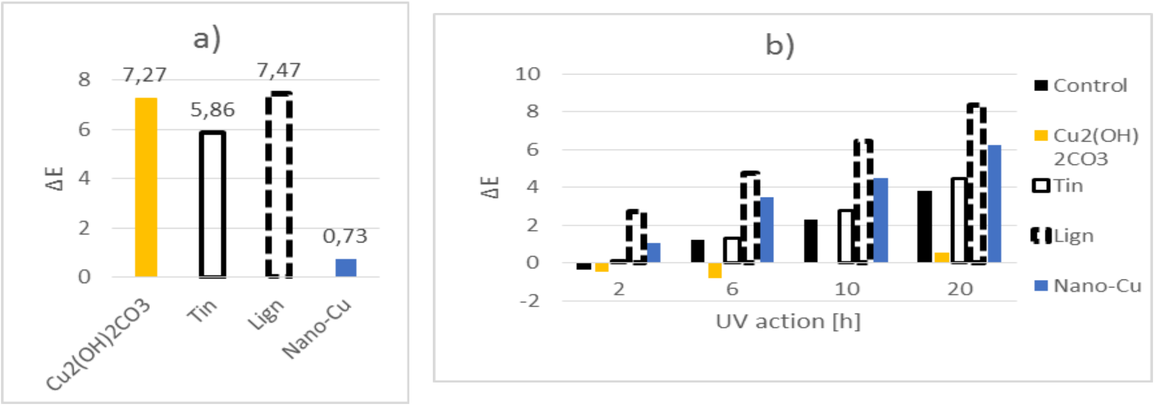

Figure 1: colour changes after wood treatment (fig 1a) and colour changes of treated wood after UV radiation (fig 1b)

INTRODUCTION

Colour change by UV radiation is mainly caused by sun exposure and occurs in both natural and thermally modified wood. Ayadi *et al.* (2003) showed that the characteristics of both materials is completely different. The surface of thermally modified wood changes its colour more rapidly than the surface of natural wood. However, it is quite confusing, because this kind of material is intended for outdoor use and in such cases the resistance of the colour to light exposure is an important issue.

In the literature a few methods for protecting wood against UV light and descriptions of the colour changes corresponding to these processes can be found. One of them involves lignin stabilization. Norrström (1969) showed that lignin contributes 80–95%, carbohydrates 5–20%, and extractives about 2% to the total UV absorption coefficient of wood. Lignin can absorb UV-light and form chromophores (Lin *et al.* 1970), and this process occurs through radical reactions. The chromophores are responsible for the wood colour changes (Dirckx 1987).

Another way to reduce the photodegradation of wood is to limit the penetration of UV radiation by the use of filters and radiation absorbers which usually form a transparent coating (Hill 2006). Furthermore, it is also possible to cover the wood surface with pigments. However, this process changes the natural colour of wood.

EXPERIMENTAL

Poplar wood (*Populus* spp.) in the form of samples with dimensions of 1200 x 120 x 20 mm (the last dimension along the fibers) were used for thermal modification. Wood samples were subjected to a temperature of 200°C under a steam atmosphere. The modified boards were then cut into samples with dimensions of 40 x 5 x 40 mm (the last dimension along the fibers). Poplar wood samples were treated with the above mentioned formulations by soaking (S) or painting (P) methods. The composition of photostability systems, retention of impregnation solution and treatment method are presented in Table 1.

Table 1: Composition of photostability systems, retention of impregnation solution and treatment method

Acronym	**Photostability system**	**Concentration [%]**	**Coating agent**	**Concentration [%]**	**Solvent**	**Retention g/m^2**	**Treatment method**
Control	-	-	-	-	-	-	-
Tin	Tinuvin® 5050	4	-	-	Ethanol	180	P
TinCoat	Tinuvin® 5050	4	Ftalak s 6120	15	White spirit	180	P
Lign	Lignostab	4	-	-	Water	180	P
LignCoat	Lignostab	4	Ftalak s 6120	15	White spirit	180	P
$Cu_2(OH)_2CO_3$	Copper bicarbonate	10	-	-	Water	600	P
Nano-Cu	Nano-copper	0,005	-	-	Water	23	S

Artificial ageing

Wood samples were divided into two groups before ageing, according to modified ISO 11341-1, in Solarbox 1500e chamber. The first group of samples were aged over 10 cycles. One cycle lasted 120 minutes of the following conditions: relative moisture content 65%; temperature of wood surface 65^{o}C; radiation 550 W/m^2. The second group of samples were aged for the same time (10 cycles), but one cycle included 102 minutes at the same conditions and 18 minutes of soaking in distilled water. In both cases the colour of the samples was measured before ageing and after 1, 3, 5 and 10 cycles of ageing.

Colour measurements

The measurements were done with a DataColor 600® in the CIE Lab system, characterised by five parameters: lightness L*, chromaticity coordinates a* and b*, and standard illuminance D65. On the surface of the wood samples there were 4 points marked in order to made the measurement every time at the same place. On the basis of the differences between the three components L*, a* and b*, the changes in the colour of the samples in the CIELAB system were determined (ΔE) (fig 2). It is assumed that the trained observer is able to observe the colour change when ΔE>2 and the inexperienced observer is able to observe the colour change when ΔE is more than 3.5 (ΔE>3.5).

$$\Delta E = [(\ \Delta E)^2 + (\Delta a)^2 + (\Delta b)^2]^{0,5}$$

Figure 2: The equation to calculate the colour change

The samples storage, impregnation, ageing procedure and the colour measurement were done in a climate chamber without light.

RESULTS AND DISCUSSION

Figure 3 presents the colour changes for samples during ageing with 10 cycles without water soaking. Wood treated with MF demonstrated the best protection against UV light because after 10 cycles ΔE was lower than 1 and such changes could not be observed with the human eye. Wood treated with Tin and TinCoat showed similar colour changes with ΔE = 4. The wood treated with Lign and LignCoat showed ΔE > 8 after 10 cycles, and in this case two different colours were recorded.

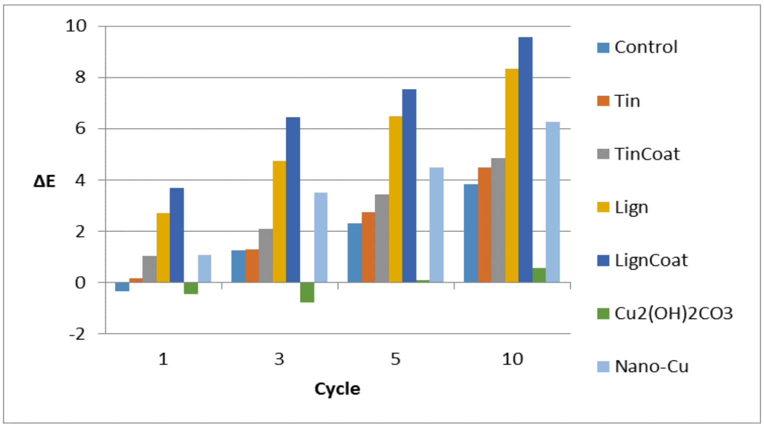

Figure 3: The colour changes of heat-treated wood during ageing test (without soaking in water)

Figure 4 presents the colour changes for samples during ageing with water soaking. Wood treated with MF showed the best protection against UV light - after 10 cycles ΔE was lower than 2. Wood treated with Lign and LignCoat changed the wood colour after 3 cycles (ΔE > 4) and wood treated with Tin and TinCoat changed the wood colour after 5 cycles (ΔE > 4). Wood treated with Nano-Cu exposed to 10 ageing cycles presented higher colour changes (ΔE = 8). Wood treated with LignCoat after 10 cycles of ageing presented the highest changes - ΔE > 12.

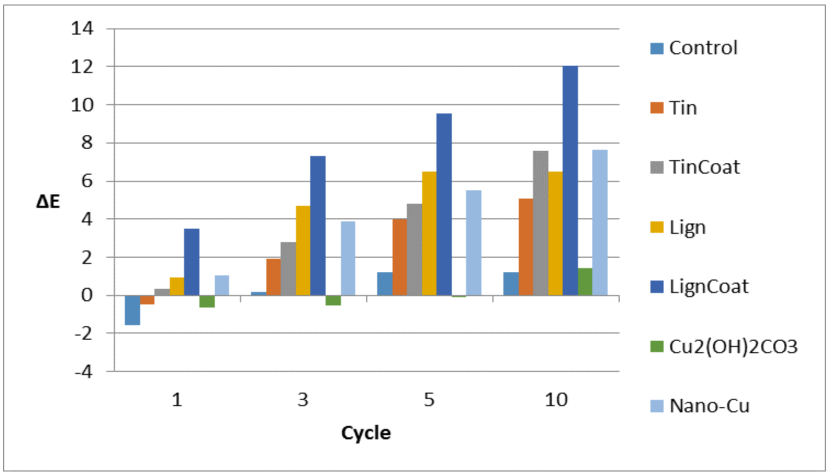

Figure 4: The colour changes of heat-treated wood during ageing test (with soaking in water)

CONCLUSIONS

The best colour stability after UV action was exhibited in wood samples treated with the model formulation, i.e. copper bicarbonate. Unfortunately this agent changed the wood colour during treatment (ΔE > 7). The investigations carried out demonstrated the potential possibilities of wood photostabilisation using the model formulation treatment. This result is similar to wood ageing with UV radiation or UV radiation and water soaking. The nano-Cu agent, as well as Tin and Lign, was not effective in protection against UV radiation. Moreover it was observed that thermally treated wood after ageing with water soaking showed better UV protection than after ageing without water soaking.

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COST Action FP1404 Fire Safe Use of Bio-Based Building Products

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Keywords: fire safety engineering, material science, structural design

ABSTRACT

Our forests are a naturally renewable resource that has been used as a principal source of bio-energy and building materials for centuries. The growth in world population has resulted in substantial increases in demand and in consumption of all raw materials. Resulting increases in the demand for wood and other bio-based products provides a unique opportunity for developing new generations of renewable, sustainable and material efficient bio-based composites. Bio-based building products have a very long history, e.g. as timber structural members. Combustibility was the main reason why bio-based building materials were banned from many applications. When Performance Based Design (PBD) became possible, many building regulations opened the market for bio-based building products. However, large differences between regulations in countries currently exist and the use of combustible building products is still very limited (e.g. in Spain bio based insulations can be used up to a building height of 18m while it is limited to 7m in Germany).

FUTURE OF BIO-BASED BUILDING PRODUCTS

Fire Safety Engineering (FSE) may be a tool to address high fire safety levels for combustible building products and in recent years FSE has found large acceptance in many countries. FSE allows a PBD with customized building solutions. FSE can be defined as the application of scientific and engineering principles to estimate the effect of fire in order to reduce the loss of life and damage to property by quantifying the risks and hazards involved and provide an optimal solution to the application of preventive or protective measures (INSTA 950 2014). However, the available techniques are often limited to non-combustible materials.

REQUIRED ENGINEERING COMPETENCE

The determination of building specific fire development, evacuation needs and active fire safety measures is normally covered by fire safety engineers while structural engineers design the load-bearing structure often by disregarding their possible interaction with the global building design. Both professions struggle with a large variation in regulations regarding material restrictions and load-bearing performance requirements in different regions and countries. Material scientists are deeply involved in the development of new products but are seldom aware of the boundary conditions given in building regulations and the field of applications. Therefore, COST Action FP1404 offers a networking platform for:

i) fire safety engineers,
ii) structural engineers and
iii) materials scientists.

FIELDS OF THE COST ACTION

There are several research questions which have to be answered for the application of FSE tools and combustible building products and lead to a harmonised European market.

In principle, at first the material characteristics of surfaces exposed to fire and the fire behaviour of the materials in the first (development or growing) phases of a fire have to be determined. Today, combustible materials are tested according to EN 13823, EN ISO 11925-2 and EN ISO 9239-1 and classified according to EN 13501-1. The European classification standard EN 13501-1 ranks construction materials in 7 classes with regard to their fire behaviour: A1, A2, B, C, D, E and F.

- A1 and A2 represent the two degrees of non-combustibility and limited combustibility, respectively;
- B-E represent products that may go to flashover in a room and at certain times;
- F means that no performance is determined;
- additional classes of smoke production (s1 to s3) and of flaming droplets/particles (do-d2) have also been introduced.

The aforementioned classes describe the *Reaction to fire* of building products. In building regulations, different rules for surface materials are specified depending on the use and type of the building. This area mainly affects fire safety engineers and material scientists.

Secondly, the overall structural performance after flash over when the fire is fully developed has to be verified by testing or by calculation (burning phase). The most important input parameter to estimate the response of elements is the fire development (fire curve). However as soon as the fire curve deviates from the *"standard fire curve"* (compare EN 1363-1), verification becomes complex or impossible. In this phase the compartment temperature is more homogenous and the fire can be ventilation controlled (limited oxygen available) or controlled by the fire load (limited fuel available). Severe fires are often ventilation controlled. When combustible gases cannot burn inside the compartment, the ignition occurs outside the compartment near the façade.

Thirdly, the last phase of a fire is the decay phase when the fuel is consumed and the temperature falls. For compartments with combustible surfaces and insulation it is today not clear if and when they will reach a burn–out, namely the condition when all fuel (e.g. furniture) is consumed and only the structure itself is left.

The requirements for fire safety in national regulations have to use the European fire classes. The nations have different requirements among the fire classes to meet the safety levels. This is because the organisational and technical fire prevention e.g. available fire brigades, necessity of sprinklers, requirements on escape routes, etc. differ from nation to nation. When performance based design (PBD) for fire was introduced, many national building regulations effectively opened the market for bio-based building products. However, the available tools, guidelines and engineering techniques are often limited to non-combustible building materials. Therefore knowledge of the performance of many bio-based building products needs to be determined and implemented in practical guidelines and engineering tools.

Work within FP1404 will be organized in a WG for Dissemination as well as in three technical WGs:

- WG1: Contribution of bio-based materials to the fire development;
- WG2: Structural elements made of bio-based building materials and detailing;
- WG3: Regulations for the fire safety of bio-based building materials.

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Understanding Wood Modification Through an Integrated Scientific and Environmental Impact Approach (COST Action FP1407)

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ABSTRACT

Though many aspects of wood modification (chemical, thermal or impregnation) treatments are known, the fundamental influence of the process on product performance, the environment, and end of life scenarios remains unknown. To contribute to a low-carbon economy and sustainable development, it is essential to integrate interactive assessment of process parameters, product properties developed, and environmental impacts. Therefore, a group of researchers proposed a new COST Action, FP1407 "Understanding wood modification through an integrated scientific and environmental impact approach", which was selected for funding in November 2014. The main objective of Action FP1407 is to characterize the relationship between wood modification processing, product properties and the associated environmental impacts, in order to maximize sustainability and minimize environmental impacts in the whole life cycle of a product. The Action will provide the critical mass of Europe-wide knowledge needed to achieve future developments in the field. Networking, multi-disciplinary exchange of knowledge and scientific excellence, as well as the expertise of industrial members, will enable comprehensive research and development to be undertaken on modification processing and product design with emphasis on their environmental impacts. This paper will briefly introduce the key research areas, work plan and secondary objectives of COST Action FP1407.

INTRODUCTION

In the last call of past COST structure, Action FP1407 "Understanding wood modification through an integrated scientific and environmental impact approach" (ModWoodLife) was selected for funding. Its MoU is available at: http://w3.cost.eu/fileadmin/domain_files/FPS/Action_FP1407/mou/FP1407-e.pdf. The Action started in March 2015 and will continue until April 2019. The main aim of the Action is to characterize the relationship between modification processing, product properties and the associated environmental impacts. This includes the development and optimization of modification processing and quantification of the impacts of emerging treatment technologies compared to traditional processing and alternative materials, to maximize sustainability and minimize environmental impacts. The Action will provide the critical mass of Europe-wide knowledge needed to achieve future developments in wood modification processing with an integrated assessment of process parameters, product properties developed and environmental impacts.

The Action has members from 24 European countries and 5 COST collaboration countries (Ukraine, USA, Canada, New Zealand, and Chile), whilst an additional 4 have expressed their intention to sign the MoU.

Reasons for the Action

The forest-based sector can become a leader in achieving the European Commission's ambitious CO_2 emission reductions goal (Roadmap 2050) with innovative production technologies, reduced energy consumption, and increased wood products recycling. The use of forest products in long life applications, such as in the built environment, allows for the possibility to extended the storage of atmospheric carbon dioxide.

The forest-based industries are continually developing advanced processes, materials and wood-based solutions to meet evolving demands and increase competitiveness. Several emerging environmental-friendly processes for wood modification (chemical, thermal and impregnation/polymerization) have been developed, which can improve the intrinsic properties of wood and provide desired form and functionality. However, a more detailed consideration reveals several issues which lead to the question: Is the global environmental impact of wood modification processing and further uses of the resulting products comparable with the impact of native, untreated wood? To address this question, COST Action FP1407 will apply the cradle to cradle (C2C) concept to the development of products based on wood modification processes. This paradigm values new advanced wood-based materials with improved intrinsic properties that promote efficient product reuse, recycling and end-of-life use, and pave the way to a low-carbon economy.

Different modification processes, with possible variations in their parameters, yield modified wood with different properties, thereby enabling the creation of different product lines. However, they also have different environmental impacts, which are consequently transferred into materials, elements, and final products. Interactive assessment of process parameters, product properties, and environmental impact should be used to aid the development of innovative modification processes and manufacturing technologies, both existing and planned, which embrace the cradle to cradle paradigm. Recycling, up-cycling and end-of-life disposal options need to be integrated in a fully developed industrial ecology. Intelligent material reuse and up-cycling concepts could reduce the amount of waste destined for landfills or down-cycling. But in order to develop and/or optimize wood modification processing to minimize environmental impacts, much more information must be gathered about relevant process factors. This includes the development of chain of custody procedures throughout the entire life cycle.

Research into wood modification processing and the resultant products must place more emphasis on the interactive assessment of process parameters, developed product properties, and environmental impacts. Energy consumption contributes considerably to the environmental impact of modified wood. However, the improved properties during the use phase might reduce the environmental impact of the modified wood product overall. It is important to note that the effective use of wood throughout its whole value chain from forest management, through multiple use cycles, and end-of-life disposal can lead to truly sustainable development.

ORGANIZATION OF THE ACTION

The Action FP1407 has 4 Working Groups (WG) that address the relevant key areas described in the MoU (http://www.cost.eu/COST_Actions/fps/Actions/FP1407):

Working Group 1: Product Category Rules - Objectives: To develop product category rules for modified wood based on the scientific and industrial state-of-the-art of commercialized and developing modified wood products and technologies. Evaluation of current PCRs and adoption where appropriate.

Working Group 2: Life Cycle Assessments - Objectives: To perform objective environmental impact assessments of commercial modification processes and incorporate environmental impact assessments into wood modification processing and product development, including recycling and upgrading at the end of service life.

Working Group 3: Environmental products declarations - Objectives: To develop environmental product declarations based on WG1 and WG2 and force a harmonization of various national EPDs in the field of wood modification.

Working Group 4: Integration, dissemination and exploitation - Objectives: To ensure dissemination, evaluation, and exploitation of the Action's results together with establishing a strong network with the relevant industrial stakeholders.

GOALS OF THE 1ST GRANT PERIOD

Action FP1407's 5 defined main goals for the 1st Grant Period (June 2015 – May 2016) are to:

- Deliver a state of the art in generic wood product Life Cycle Assessment and Environmental Products Declarations in different Member States
- Perform a systematic comparison of modification processes including their technical characteristics and environmental performance
- Deliver a state of the art of the life cycle analyses of different commercial modification processes ("cradle to gate" and "cradle to grave") and examine scenarios for the service life and end of life of wood products
- Explore possibilities to prepare a joint book to be put forward for publishing in the Springer Series "Environmental Footprints and Eco-design of Products and Processes".
- Recruit industrial stakeholders to take part in a Special exploitation committee of Action FP1407, which will promote dissemination and commercialization of knowledge acquired in Action FP1407.

IMPACT OF THE ACTION

Networking, open discussion, planning and collaboration within the Action will provide the most productive, most proficient and most enduring tactic to build relationships amongst researchers from COST countries, COST Inclusiveness countries and COST Near Neighbouring countries working on the topics of this Action and therefore lead to a positive transformation in the wood-based products sector. Furthermore, strong emphasis on the involvement of Early Stage Researchers and gender balance will have an impact on the future development of the sector in COST countries. High levels of participation will be encouraged to ensure these objectives are met through the use of inclusive measures at meetings.

The expected scientific impacts will be the results of coordination and streamlining of profound scientific investigations on the basics of wood modification processing and modified wood, which will be used in industry for an improvement and optimization of existing technologies and the development of new modification processes, as well as the development of Product Category Rules and life cycle models for modified wood. Besides the networking and collaboration based on current projects in the COST countries, this Action will result in new international and interdisciplinary project proposals, as well as the development of new standards.

CONCLUSION

The main aim and objectives of the Action FP1407 is to advance research in the field of wood modification to allow significant contributions to the goals of European and global resource efficiency and a low carbon economy. These goals will be met by implementing excellent research in the area of wood modification, properties of modified wood, and environmental impacts. The interactive assessment of process parameters, product properties and environmental impacts performed in this Action will build on the previous scientific and technical research in environmental assessment and wood modification. Action FP1407 will bring together knowledge, expertise, and infrastructure to achieve the Action's aim. Current knowledge will be upgraded and known challenges overcome. The goals of sustainable development to increase economic efficiency, protect, and restore ecological systems and improve human well-being, or a combination of the three are expected to lead to new concepts, products, and processes optimizing the multiple utilization/recycling of forest-based resources. Life cycle analysis, industrial ecology and the cradle-to-cradle concepts will be used as key tools in economic developments also leading to new business opportunities through innovative products with properties optimized to the end use requirements and the sustainable use of resources. It is emphasized that this work has to also extend to unmodified timber products, since baseline comparisons have to be made. This greatly extends the range and impact of the Action beyond the wood modification industries.

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MORE INFORMATION

COST Action FP1407 web page: http://costfp1407.iam.upr.si/en/

SESSION FOUR

Chemical Modification

Acetylation of German Hardwoods

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ABSTRACT

New approaches to silviculture in Germany call for a maximum increase of biodiversity in forests through the creation of mixed forests. Lower Saxony, for example, strives for a 65% share of deciduous trees. This conflicts with the pattern of consumption of lumber, which in Germany is currently met with about 80% coniferous lumber. Against this background it will be necessary to use deciduous trees more extensively to meet the future demand of the industry. As part of a larger research program the feasibility of acetylating German hardwoods to enhance their performance was studied. Beech (*Fagus sylvatica*), alder (*Alnus glutinosa*), lime (*Tilia* spp.) and maple (*Acer* spp.) were acetylated in an adapted industrial process at Accsys Technologies to high Weight Percent Gains in commercial sizes. The resistance against fungal decay (in a test adapted to CEN/TS 15083-1 for *Rhodonia* (*Poria) placenta* and *Trametes versiolor*) showed very low mass losses for the acetylated woods as would be expected based on the literature about the potential of acetylation to improve durability. Also cyclic dimensional stability tests (ASE) were in accordance with the literature and indicated highly stable acetylated wood species in changing moisture conditions. In addition, the mechanical properties (hardness, bending properties) of acetylated woods were determined. The results overall are very promising and upscale efforts to demonstrate uniformity and reproducibility of the acetylated hardwoods would be the next step.

INTRODUCTION

Wood is a renewable, biodegradable and sustainable matrix of cellulose, hemicelluloses, lignin, extractives and inorganics. Nature is programmed to recycle it, in a timely way, back into its basic building blocks of carbon dioxide and water through biological, thermal, aqueous, photochemical, chemical and mechanical degradation processes. Many problems are associated with wood destroying fungi under high humidity conditions. Furthermore, wood alters its dimensions with changing moisture content. Wood exposed to moisture is frequently not at equilibrium, having wetter areas and drier areas within the same board. This exacerbates the moisture problem resulting in differential swelling followed by cracking and/or compression set.

European hardwoods are mainly used indoors because of poor dimensional stability and low resistance to basidiomycetes. Nevertheless utilization in new fields of application might be possible if these drawbacks could be overcome.

Regulations on the use of biocides to enhance the durability of wood species are increasing. Environmentally friendly alternatives are chemical modifications, which result in improved wood performance. By altering the wood matrix at a molecular level, the properties of wood species with low durability can be enhanced. Acetylation is well known to increase the resistance of wood to wood decaying fungi and destructive insects, as well as improving the dimensional stability in moist conditions (Alexander *et al*. 2014, Beckers *et al*. 1994, Bongers *et al*. 2015, Goldstein *et al*. 1961, Larsson-Brelid *et al*. 2000, Larsson-Brelid and Westin 2010, Militz 1991, Papadopoulos and Hill 2002, Papadopoulos *et al*. 2008, Rowell and Dickerson 2014).

Wood acetylation

Acetylation has been studied extensively and has been shown to be one of the promising methods for improving the technical properties of low durability wood species. Fuchs (1928) did the first wood acetylation trial on small blocks using acetic anhydride and sulphuric acid as a catalyst. Since then many others have performed research on the acetylation of wood, with respect to the process as well as the material properties of acetylated wood. A comprehensive background to acetylation and wood modification in general is given by Hill (2006), Rowell (2006), Homan and Jorissen (2004) and Jones (2007).

In the last decade most work has been done with uncatalyzed acetic anhydride. 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 acetic acid as a by-product (see Figure 1). Accsys Technologies introduced an acetylated wood product named Accoya® wood (www.accoya.com) into the market in 2007. Accoya® wood is based on the acetylation of radiata pine (*Pinus radiata* D. Don) and is mainly used for non-structural applications such as joinery, cladding, decking and (light) civil works in the Netherlands, UK and Germany (Alexander 2007, Bongers *et al*. 2009).

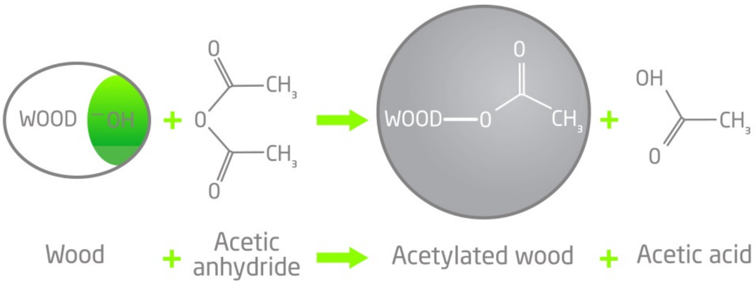

Figure 1: Schematic reaction of acetic anhydride with wood

Currently Accsys Technologies is working on the development of commercially viable acetylation processes for additional wood species. Included in this research program are various wood species sourced throughout the world. Furthermore, with respect to commercial production, the available volume, quality, and sawn wood pricing of the species are important considerations. In addition to process development, detailed studies are performed on the wood characteristics, economics and market opportunities.

Acetylation of European hardwoods

New approaches to silviculture in Germany call for a maximum increase of biodiversity in forests through the creation of mixed forests. Lower Saxony, for example, strives for a 65% share of deciduous trees. This conflicts with the pattern of consumption of lumber, which in Germany is currently met with about 80% coniferous lumber. Against this background, it will be necessary to use deciduous trees more extensively to meet future demand. As part of a larger research program the feasibility of acetylating European hardwoods to enhance performance was studied. Beech (*Fagus sylvatica*), alder (*Alnus glutinosa*), lime (*Tilia* spp.) and maple (*Acer* spp.) were acetylated in an adapted process to high Weight Percent Gains in commercial sizes.

The untreated and acetylated wood species were subjected to different performance tests:

- resistance against fungal decay according to CEN/TS 15083-1 for *Rhodonia* (*Poria*) *placenta* and *Trametes versicolor*
- cyclic dimensional stability tests
- mechanical properties (Brinell hardness, bending strength and stiffness)

MATERIALS AND METHODS

Square edge boards were sawn out of stems obtained from the European forest. The boards were kiln dried and cut in half. One part of the board was acetylated and the other remained untreated for reference.

Modification

Commercial sized boards of beech (*Fagus sylvatica*), alder (*Alnus glutinosa*) lime (*Tilia* spp.) and maple (*Acer* spp.) were acetylated in the plant of Accsys Technologies in Arnhem, the Netherlands.

An overview of the boards is shown in Table 1**.**

Table 1: Overview of the boards acetylated

Wood species	Amount	Thickness [mm]	Width [mm]	Length [m]
Beech	40	35	110-190	2
Alder	40	35	100-200	2
Lime	41	36	95-220	2
Maple	36	36	120-270	2

Prior to and after the acetylation the dimensions and weight of the boards was measured. The wood moisture contents were measured with a pin-type electric moisture meter prior to acetylation. The data was used to calculate the (ovendry) densities of the untreated and acetylated woods. A 6 cm piece was cut from 5 boards per wood species and weighed prior to and after the acetylation to calculate the Weight Percent Gain (WPG) of the acetylation treatment. After acetylation the residual acetic acid content was determined by the internal QC method of Accsys Technologies.

Resistance against fungal decay

From 7 randomly selected boards, 30 samples (50x25x15mm^2) per wood species (beech, lime, alder, and maple) were cut by the University of Göttingen from the middle of the boards and according to the requirements of the standard (annual ring orientation).

All test specimens were leached according to the EN 84 leaching test. After this leaching procedure, the specimens were oven dried and conditioned at 20°C and 65% relative humidity (RH) to equilibrium moisture content. To perform the durability test, the specimens were placed in culture vessels, which contained sterilised malt extract agar nutrient medium (MEA) and were inoculated with following test fungi:

- *Rhodonia (Poria) placenta* (*R. placenta*), brown rot
- *Trametes versicolor* (*T. versicolor*), white rot

As untreated reference specimens, the same wood species were tested. Virulence samples were made from beech (*Fagus sylvatica*) for *T. versicolor* and Scots pine sapwood (*Pinus sylvestris*) for *R. placenta.* All culture vessels were placed in a culture room (22 °C/70% RH) for a period of 16 weeks. After the exposure period, the specimens were removed from the culture vessels and weighed directly after harvesting and after drying at 103°C for 24 hours. Finally the mass loss of each individual specimen due to fungal decay was calculated based on the dry weight before and after the test. The durability was classified according to CEN/TS 15083-1 (2005) by median mass loss.

Table 2: Durability classification according to CEN/TS 15083-1

Durability class	**Description**	**Median mass loss [%]**
1	Very durable	≤ 5
2	Durable	>5 to ≤ 10
3	Moderately durable	>10 to ≤ 15
4	Slightly durable	>15 to ≤ 30
5	Not durable	>30

Cyclic dimensional stability (ASE)

The ASE (**A**nti **S**well **E**fficiency) describes the swelling performance of treated samples compared to untreated samples. Ten treated and untreated samples (25x25x10mm³) from each wood species were cut from the middle of 10 randomly selected boards. The ASE was determined according to Hill and Jones (1996). During this test, the samples were cyclically saturated with water (1 hour at 80 mbar, storage in water for 24 hours) and subsequently dried in an oven at 103 °C for 24 hours. After each water saturation- and drying step the dimensions were determined. A cycle was completed when the samples were anhydrous after a drying process of several days.

Mechanical properties

The Brinell hardness and bending properties (MOR and MOE) were determined according to the standards shown in Table 3. For hardness, 10 defect free samples (3 measurements per sample) of each wood species were tested. The bending properties were determined on 30 specimens. All tests were performed on a universal testing machine (ZWICK GmbH und Co. KG, Ulm Germany) with a 10 kN load cell. The results were evaluated with TESTEXPERT II software (ZWICK GmbH und Co. KG, Ulm Germany). Prior to testing, all test specimens were conditioned at 20 °C and 65% RH. The wood moisture content and density of each sample was determined.

Table 3: Performed mechanical tests, test machines, samples sizes and used standards for performed mechanical properties

	Test machine and maximum load	**Sample size (rad x tang x long)**	**Standard Number and Year**
Hardness, radial [N/mm^2]	ZWICK 10kN	25x50x50 mm^3	EN 1534 (2000)
MOR [N/mm^2]	ZWICK 10kN	10x10x180 mm^3	DIN 52 186 (1975)
MOE [N/mm^2]	ZWICK 10kN	10x10x180 mm^3	DIN 52 377 (1978)

RESULTS & DISCUSSION

Acetylation

A summary of the results is shown in Table 4. The results look very promising for maple and alder. Overall good acetylation levels and a low amount of wood checking are shown. The lime showed spots that were known to be less acetylated, and therefore the performance of the material could be less uniform. It is known that further adapted process parameters or a limitation in board width is needed for the acetylation of a highly unstable wood species like beech. Since the process was not adapted the acetylated beech showed a high amount of surface checks, but in general the degree of modification was uniform to high levels.

Table 4: density, WPG, Acetic acid content and wood quality after acetylation process

Wood species	**Oven dried density [kg/m^3]***		**WPG [%]***	**Acetic acid content [%]***	**Wood quality after acetylation**
	Untreated	**Acetylated**			
Beech	695 (655 - 725)	770 (740 - 805)	20.7 (19.8 - 21.2)	0.5 (0.4 - 0.9)	35% of boards with surface checks, ranging from 3 cm up to 173 cm in a board.
Alder	465 (385 - 515)	530 (420 - 610)	23.4 (22.7 - 24.1)	0.3 (0.2 - 0.3)	11% of the boards with surface checks, ranging from 19 cm up to 42 cm in a board.
Lime	460 (340 - 550)	520 (360 - 630)	19.3 (19.2 - 19.5)	0.4 (0.3 - 0.5)	30% of the boards with surface checks, ranging from 3 cm up to 97 cm in a board.
Maple	550 (520 - 600)	645 (595-690)	20.0 (13.9 - 22.8)	0.4 (0.2 - 0.6)	No surface checks

** average (minimum – maximum)*

Resistance against fungal decay

The test results are valid. The reference controls (n=30) reached the required minimum value for the mean loss in mass of 20% for the test fungus (Table 5).

Table 5: Density, mass loss and moisture content of virulence samples dependent on test fungus

Wood species	**Fungus**	**density * [kg/m^3]**	**mass loss* [%]**	**moisture content* [%]**
Beech	*T. versicolor*	700	27,73	59,12
Scots pine sapwood	*R. placenta*	485	23.91	102.93

*mean values

The mass loss of treated specimens compared to untreated samples indicates a significant increase in durability (Table 6 and 7).

Table 6: Results of fungal decay test for R. placenta

Wood species	Treatment	Mean density [kg/m³]	Median mass loss [%]	Mean mass loss [%]	Mean moisture content [%]
Beech	acetylated	791	0,15	0,23	21,79
	untreated	692	17,47	17,41	80,82
Alder	acetylated	557	-0,13	-0,05	28,55
	untreated	413	27,18	25,90	90,80
Lime	acetylated	556	0,10	0,11	37,69
	untreated	542	24,75	26,09	83,30
Maple	acetylated	660	-0,06	0,02	29,37
	untreated	576	22,47	22,64	77,95

Table 7: Results of fungal decay test for T. versicolor

Wood species	Treatment	Mean density [kg/m³]	Median mass loss [%]	Mean mass loss [%]	Mean moisture content [%]
Beech	acetylated	792	0.14	0.13	24,75
	untreated	700	27,54	27,73	59,12
Alder	acetylated	561	0,13	0,14	30,34
	untreated	414	34,39	35,25	69,65
Lime	acetylated	560	1,11	0,93	28,49
	untreated	546	26,93	27,43	53,61
Maple	acetylated	666	0,11	0,14	39,13
	untreated	568	31,95	32,21	60,26

In Table 8 the durability classes (DC) according to CEN/TS 15083-1 are given. The untreated wood species have a DC of 4 or 5. By acetylation they are all upgraded to DC 1.

Table 8: Durability class of treated and untreated wood species according to CEN/TS 15083-1

Wood species	Treatment	Durability class
Beech	acetylated	1
	untreated	5
Alder	acetylated	1
	untreated	5
Lime	acetylated	1
	untreated	4
Maple	acetylated	1
	untreated	5

Cyclic dimensional stability (ASE)

A significantly reduced swelling rate was seen for the acetylated wood species (see Figure 2). This results in high ASE values (76 and 82%), even after 10 cycles of water saturated and ovendry condition (see Figure 3).

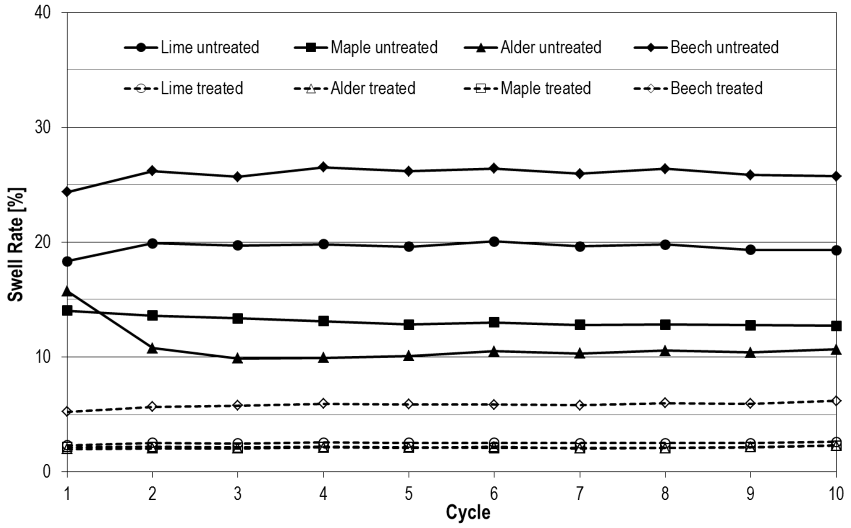

Figure 2: Swell rate [%]of treated and untreated wood species

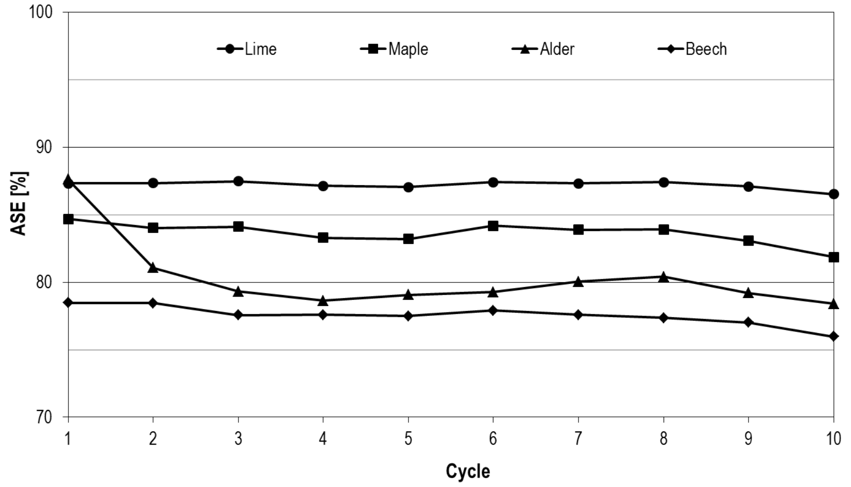

Figure 3: ASE [%] of treated and untreated wood species

Mechanical properties

In Table 9 the Brinell hardness results are shown. A statistically significant increase in average hardness was seen for all acetylated wood species, except for lime (see Table 11) even though this had a higher average Brinell hardness compared to the untreated control. The acetylation process resulted in a significant decrease in moisture content and an increase in average MOR compared to the untreated samples (Table 10 and Table 11) for all wood species tested. The average MOE did not change significantly for alder, lime and maple, but had a 9.6% increase for beech (Table 10 and Table 11).

Table 9: Results of Brinell hardness measurements for acetylated and untreated samples

Wood species	Treatment	Density* [g/cm³]	Moisture content* [%]	Hardness* [N/mm^2]
Beech	acetylated	0,79 (0,01)	4,64 (0,09)	62,14 (5,81)
	untreated	0,79 (0,01)	11,52 (0,21	50,55 (62,14)
Alder	acetylated	0,48 (0,02)	2,89 (0,10)	22,85 (2,30)
	untreated	0,45 (0,01)	12,42 (0,10)	16,52 (2,69)
Lime	acetylated	0,55 (0,01)	2,84 (0,11)	29,34 (4,83)
	untreated	0,60 (0,01)	10,72 (0,16)	26,82 (2,22)
Maple	acetylated	0,66 (0,02)	3,55 (0,06)	57,77 (7,82)
	untreated	0,62 (0,01)	12,42 (0,32)	37,60 (2,11)

* *Mean values and standard deviation*

Table 10: Density, moisture content MOE and MOR of acetylated and untreated samples

Wood species	Treatment	Density* [g/cm³]	Moisture content* [%]	MOE* [N/mm^2]	MOR* [N/mm^2]
Beech	acetylated	0,80 (0,02)	4,14 (0,15)	16189 (1659)	145,3 (22,1)
	untreated	0,77 (0,04)	12,15 (0,33)	14631 (13,51)	129,2 (19,7)
Alder	acetylated	0,52 (0,05)	2,72 (0,19)	8351 (1312)	83,8 (12,9)
	untreated	0,48 (0,04)	11,94 (0,25)	8616 (1339)	72,6 (10,7)
Lime	acetylated	0,51 (0,04)	2,52 (0,13)	11507 (7759	106,1 (1,7)
	untreated	0,59 (0,02)	11,30 (0,26)	11583 (978)	88,5 (6,9)
Maple	acetylated	0,67 (0,01)	3,26 (0,09)	12516 (2432)	129,2 (19,7)
	untreated	0,64 (0,02)	12,82 (0,37)	12790 (908)	107,3 (5,1)

* *Mean values and standard deviation*

Table 11: Average change of mechanical properties due to acetylation

Wood species	Δ Hardness		Δ MOR		Δ MOE	
	[%]	Significant differences*	[%]	Significant differences*	[%]	Significant differences*
Beech	+23,0	Yes	+12,8	Yes	+9,6	Yes
Alder	+38,8	Yes	+13,7	Yes	-3,5	No
Lime	+9,30	No	+19,1	Yes	-0,9	No
Maple	+53,7	Yes	+19,6	Yes	-3,1	No

* *Student t-test*

CONCLUSIONS

The resistance against fungal decay according to CEN/TS 15083-1 for *Rhodonia* (*Poria*) *placenta* and *Trametes versicolor* showed very low mass losses for all acetylated wood species (beech, alder, lime and maple). All were classified as being in Durability Class 1. The cyclic dimensional stability tests (ASE) also indicated highly stable acetylated wood species under changing moisture conditions. In addition, the mechanical properties showed an increase in average hardness and MOR whereas the MOE remained unchanged. In summary, the results of the acetylation of beech, alder, lime and maple are overall very promising and upscaling efforts to demonstrate uniformity and reproducibility will be the next step.

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Covalent Fixation of Boron in Wood through Transesterification Reaction with Boron-Bearing Vinyl Ester

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Keywords: boronated wood; carboxyphenylboronic acid penacol ester; durability; transesterification.

ABSTRACT

The goal of this research was to covalently introduce boron into wood using a boron-bearing vinyl ester as a reagent and assess the durability of the treated wood. Vinyl ester of 4-carboxyphenylboronic acid was synthesized and used as a reactive reagent for the permanent fixation of boron in wood. The covalent incorporation of boron into the wood was achieved through a transesterification reaction between the wood hydroxyl groups and boronic vinyl ester. The synthesis of boronic vinyl ester was accomplished by the exchange reaction of vinyl acetate with 4-carboxyphenylboronic acid. The transesterification reaction between the wood hydroxyl groups and boronic vinyl ester was confirmed by FTIR spectroscopy, weight percentage gain (WPG) and by curcumin staining. By staining, a red coloration was observed caused by the formation of a boron-curcumin complex. The decay resistance of the modified wood samples was assessed by exposing unmodified and modified mini-blocks of wood to the brown rot fungi *Postia placanta, Coniophora puteana, Gloeophyllum trabeum* and a white rot fungus *Trametes versicolor* for 12 weeks. The results showed that the modified samples were very resistant to decay.

INTRODUCTION

Boron compounds are known to act as both insecticide and fungicide and have been shown to be very effective in protecting wood (Yalinkilic *et al.* 1999; Pizzi and Baecker 1996). In particular, they exhibit low toxicity against humans and are odourless, colourless and non-corrosive. However, a major disadvantage of using borates is that they are easily leached out when wood is exposed outdoor (Yalinkilic *et al.* 1999, Yalinkilic *et al.* 1998, Colakoglu *et al.* 2003). Several strategies to reduce leaching and increase the potential range of products to cover the entire spectrum of wood preservation have been proposed. All these studies suggest fixing the boron compounds within treated timber. Obanda *et al*. (2008) and Caldeira (2010) have summarized most of the alternatives that have been investigated to reduce the leachability of boron from treated wood. These strategies include surface treatments (Homan *et al*. 1995, Hedley *et al*. 2006), precipitation of organo-borate salts (Lin *et al.* 2001), a combination of biocides and non-biocidal additives (Kartal *et al*. 2003), in-situ polymerisation (Yalinkilic *et al.* 1998a; Ozaki *et al*. 2001, Baysal *et al.* 2004; Mourant *et al*. 2009; Temiz *et al.* 2008), and treatments with boron-silicon compounds (Kazunobu 1995; Yamaguchi 2003; 2005). Other strategies include the use of borates as additives in other formulations (Pohleven *et al.* 2006; McIntyre *et al.* 2011), treatments with organo-compounds (Liu *et al.* 1994; Yalinkilic *et al.* 1998b) and, recently, a combination of impregnation with borax and heat treatment (Salman *et al*. 2014). Most of the above-mentioned approaches cannot prevent the leaching of boron or the proposed formulations have penetration problems. Namyslo and Kaufmann (2009) suggested an alternative protection procedure which consists in the covalent attachment of a metalloid substituent via a benzotriazolyl-activated benzoic acid to the wood hydroxyl groups. This method is interesting, but the activated reactant is quite bulky, which may limit both the penetration and the grafting yield in wood.

The present study demonstrates a procedure for the immobilization of boron based on vinyl ester reactants for the grafting of organoboron compounds. First the synthesis of boronic vinyl ester by the transvinylation of 4-carboxyphenylboronic acid with vinyl acetate was required. The synthesized organoboron vinyl ester was then used to functionalize wood through a transesterification reaction between a synthesized organoboron vinyl ester and the hydroxyl groups of wood, using potassium carbonate as catalyst. The reactions were performed on mini blocks of Scots pine sapwood and the wood chemical modification was characterized by FTIR spectroscopy, calculation of the weight percentage gain (WPG) and curcumin staining.

EXPERIMENTAL

Synthesis of reagent

The precursor, boronic vinyl ester was synthesized by mixing 10 g (40.30 mmol) 4-carboxyphenylboronic acid pinacol ester with a 10 eq excess of vinyl acetate (VAc) in a three-neck round bottom glass flask equipped with a reflux condenser and thermometer and thereafter degassed with argon. The catalyst ($[Ir(cod)Cl]_2$, 0.01 eq), along with sodium acetate (0.03 eq) were then added and the reaction mixture was kept under magnetic stirring in a dry argon atmosphere at 100°C for 16 h. After reaction, the mixture was poured into water, extracted with dichloromethane, and the organic fraction dried over anhydrous sodium sulphate before removing the solvent in a rotary evaporator. The residue obtained was characterized by FTIR-ATR and NMR spectroscopy.

Wood treatment

Mini block Scots pine sapwood samples of 5 × 10 × 15 mm, were first extracted in a Soxhlet apparatus with a mixture of toluene and ethanol (2:1/v: v) for 8 h and then with water for additional 8 h, to remove all extractives. The wood samples were then oven-dried at 105°C for 16 h and cooled to ambient temperature in a laboratory desiccator. For each reaction, a set of dry mini blocks (25 replicates) were introduced into a flat-bottomed flask equipped with a condenser and magnetic stirrer. For each reaction, the samples were vacuum impregnated (reduced pressure of 0.8 bar for 10 minutes) with a treatment solution containing 7 mmol of boronic vinyl ester per 1 g of wood, 0.45g K_2CO_3 (catalyst) and 50 mL of NMP. All reactions were performed at 110°C for 2 and 6 h to obtain 3 and 7% weight percentage gains. After each reaction the modified samples were Soxhlet extracted with water for 2 h to remove the K_2CO_3 catalyst and then with toluene/ethanol/acetone (4:1:1 v:v:v) for an additional 8 h to remove non-bonded chemicals. The percentage weight gains (WPG) of the treated and extracted samples were then calculated.

FTIR and staining analyses

IR instrument

Infrared absorption spectra of treated and unmodified wood samples were obtained using a Spectrum Two FTIR (Perkin-Elmer) equipped with an UATR Diamond accessory, which allows collection of FTIR spectra directly from a sample without any special preparation. The "pressure arm" of the instrument was used to apply a constant pressure (monitored by software) to the sample positioned on top of the Diamond crystal to ensure good contact between the sample and the incident IR beam. All FTIR spectra were collected at a spectrum resolution of 4 cm^{-1}, with 32 scans over the range 4000 cm^{-1} to 650 cm^{-1}.

Curcumin staining (boron stain)

To confirm the introduction of boron in wood, wood samples were stained before and after treatments with curcumin reagent according to the standard method described in the American Wood Protection Association (AWPA A3-08). Additionally, one sample was taken after treatment and split evenly along the grain into two parts and the transverse sections of the treated and untreated samples (≈ 40 µm) were cut with a Leitz sliding microtome (Leitz, Wetzlar, Germany) and stained. After mounting in 50% (v/v) glycerol in distilled water, the sections were examined by a Leica DMLB LM (Leica, Wetzlar, Germany) microscope.

Decay test

Sterile culture medium (20 mL), prepared from malt (15 g) and agar (15 g) in distilled water (1 L), was placed in Ø 9 cm Petri dishes, inoculated with a small piece of mycelium of a freshly grown pure culture of brown rot fungi (*Postia placenta* FPRL 280, *Coniophora puteana* BAM Ebw.15, and *Gloeophyllum trabeum* BAM Ebw. 109) and a white rot fungus (*Trametes versicolor* CBT 863A) and incubated for 2 weeks at 22°C and 75% HR to allow full colonization of the medium by the mycelium. Two blocks (one treated and one control) were placed directly on the malt agar medium in each Petri dish. Incubation was carried out for 12 weeks at 22°C under controlled humidity conditions of 75% RH in a climatic chamber. After this period, the wood samples were cleaned, their oven dry mass determined and the mass loss calculated. The test was performed with five replicates for each fungus.

RESULTS AND DISCUSSION

For comparison with previously published acetylation by means of vinyl acetate (Jebrane and Sèbe 2007, 2008), the corresponding vinyl ester of boron-bearing precursor was synthesised. The preparation of this vinyl ester was accomplished by exchange reaction of vinyl acetate with a commercially available 4-Carboxyphenylboronic acid pinacol ester according to the scheme shown in Figure 1.

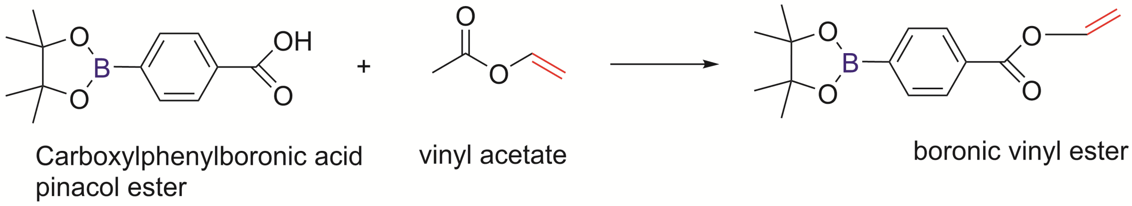

Figure 1: General reaction scheme for the synthesis of boronic vinyl ester

The structure of the synthesised boronic vinyl ester was confirmed by both FTIR and NMR spectroscopy (spectra not shown).

The transesterification reaction between wood blocks and boronic vinyl ester is shown in figure 2. During this process, the vinyl alcohol formed tautomerizes to acetaldehyde and the equilibrium is shifted to the formation of boronated wood (Figure 2). The reaction was performed on Scots pine solid wood, with N-Methyl-2-pyrrolidone (NMP) as solvent and potassium carbonate as catalyst. The reactions were performed at 110°C for 2 and 6 h. Under these conditions, weight percentage gains (WPG) of 3.2% and 7.17% were measured respectively. The functionalization of wood was confirmed by FTIR (as illustrated in Figure 3) through the emergence of new characteristic vibrations of the grafted moieties. Namely, the carbonyl stretching vibration at 1722 cm^{-1} ($\nu_{C=O}$), the C-O stretching vibrations at 1270 cm^{-1} (ν_{C-O}), and methyl vibrations at 2953 and 2870 cm^{-1} (ν_{C-H}), and 854 cm^{-1} (γ_{C-H}). Some new characteristic vibrations of the grafted phenylboronic moieties were identified namely the strong skeletal bands for aromatics at 1609 and 773 cm^{-1}. Additionally, a new vibration arose at 1190 cm^{-1}, which is a characteristic band of phenyl ester group.

Similar results were reported by Namyslo and Kaufmann (2009), when organoboron compounds were synthesized and successfully grafted in wood by esterification via benzotriazolyl-activated carboxylic acid group (Namyslo and Kaufmann 2009). Compared to boronic anhydride synthesised by Namyslo and Kauffmann (2009), the present method uses boronic vinyl ester which is not bulky and can easily penetrate the wood cell wall. In addition, the vinyl alcohol formed during the process of esterification tautomerizes to acetaldehyde and the equilibrium is shifted to the formation of boronated wood (Figure 2).

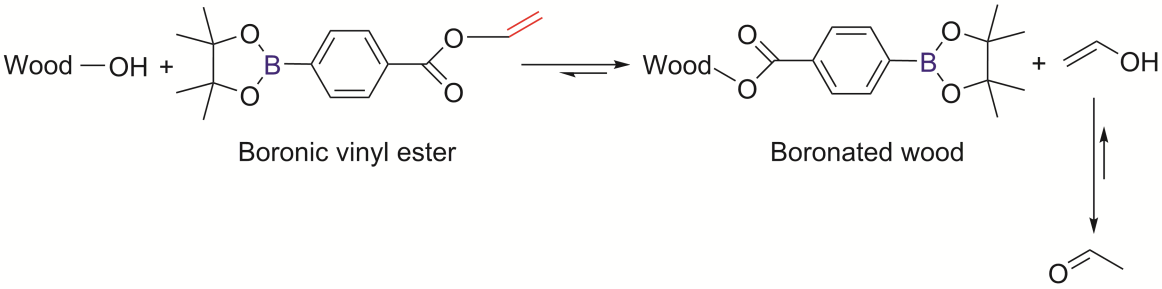

Figure 2: functionalisation of wood by transesterification reaction between wood hydroxyl groups and boronic vinyl ester

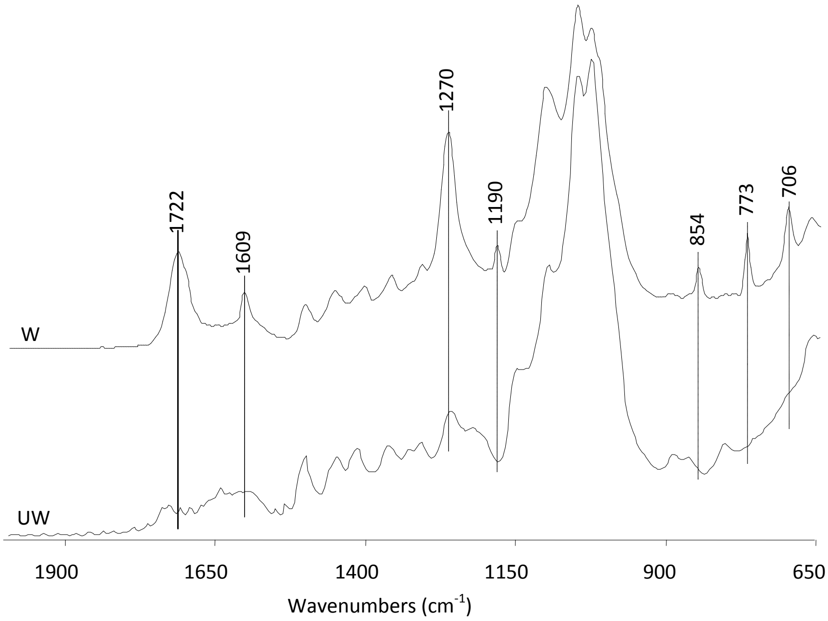

Figure 3: FTIR spectra of unmodified wood (UW), and wood esterified by boronic vinyl ester

The covalent grafting of boron into the wood was further confirmed by curcumin staining (as illustrated in Figure 4). Modified and unmodified wood samples were stained using the curcumin method described by Smith et al. (1969) and in AWPA standard A3-05 (AWPA 2008). After functionalization, the wood colour was changed from white to brown as a result of modification (Figure 4b). After staining with curcumin dye, the colour of the untreated wood shifted from white to orange/yellow (Figure 4a), while the colour in modified wood changed from brownish to reddish (Figure 4c). Early- (not shown) and latewood regions in modified wood without staining showed an overall yellow colour (Figure 4d). After staining with curcumin, the colour of both early- (not shown) and latewood changed from yellow to red (Figure 4e). This confirms that a significant amount of chemicals remained bonded in the wood after extensive extraction with an appropriate solvent.

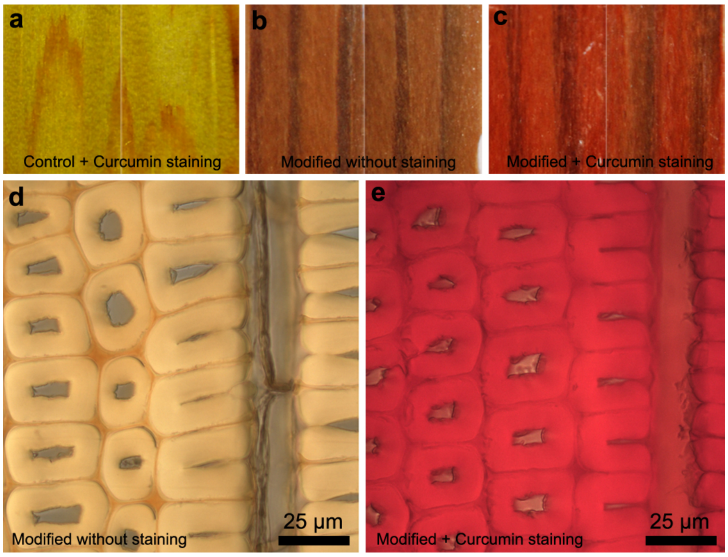

Figure 4: Photographs of wood blocks stained with curcumin before modification (a), after modification without staining (b) and after modification and staining (c); light microscopy observations of latewood cells before (d, e). Scale bar = 25 µm.

Table 1 presents the mass loss of treated and untreated samples for each studied fungi. Twelve weeks of exposure to brown rot and white rot resulted in a significant mass loss of the control, unmodified samples, indicating that both brown rot and white rot fungi were active. After 12 weeks exposure to all the fungi studied, a mass loss of less than 4% was measured in all modified samples even at low WPG (i.e 3.2%). However, it is difficult to prove whether the observed protection was imparted to the wood by boron or by the substitution of hydroxyl groups with bonded ester moieties in the cell wall that occupies space that would normally be available to water or by a combination of both effects.

Table 1: Mass loss of modified and control samples after decay test. Each measurement is an average of 5 samples (standard deviation in parentheses).

WPG	Mass loss %			
	P. placenta	*G. trabeum*	*C. puteana*	*T. versicolor*
3.2	3.8 (0.6)	1.8 (1.1)	2.3 (1.1)	3.6 (0.8)
-	24.0 (6.6)	15.0 (0.2)	16.1 (1.8)	15.3 (1.4)
7.17	2.5 (1.2)	1.4 (0.3)	1.6 (0.9)	1.8 (0.2)
-	31.2 (2.4)	19.2 (2.9)	20.7 (1.8)	16.7 (1.9)

CONCLUSIONS

In the present work, a new approach to permanently immobilize boron in the wood was developed. The concept developed comprises a synthesis of boron-bearing vinyl ester from vinyl acetate and 4-carboxyphenylboronic acid; followed by a covalent incorporation of the boron compound onto the wood via a transesterification reaction between the wood hydroxyl groups and the synthesized boronic vinyl ester. The grafting of the phenylboron moieties in wood after extensive extraction with water and organic solvent has been confirmed by WPG calculations, FTIR spectroscopy, and curcumin staining combined with light microscopy observations. Under the conditions studied, a WPG of 7.17 % was measured, indicating that a significant amount of chemical remained bonded in the wood. Modified wood samples were subsequently tested in decay trials with mini-blocks test. The results indicated that the modification was very effective at protecting wood against all four *Basidomycete* fungi investigated even at WPG as low as 3%.

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Predicting the Pore-Filling Ratio in Lumen Impregnation from Weight Percentage Gain and Densities of Wood

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Keywords: lumen impregnation, pore-filling ratio, porosity, pycnometry, apparent density, inaccessible density, weight percentage gain

ABSTRACT

Lumen impregnation, unlike most wood modification methods, is assessed by pore-filling ratio (PFR) after treatment, rather than the commonly used weight percentage gain (WPG), since the impregnant acts on the void part of wood rather than on the mass part. However, PFR cannot be measured as easily as weight during processing. Herein, we derive PFR from WPG by introducing the apparent density of untreated wood, which can be easily obtained from the bulk weight and volume of wood. The relationship between WPG and apparent density is effective and experimentally-validated by the impregnation of Sitka spruce with methacrylate monomers. Based on this evaluation method, we can study the effect of different process-related parameters on lumen impregnation. The effect of specimen length on impregnation is negligible in the range of our study; the hydraulic pressure during processing shows some effect: higher pressure leads to higher PFR. Impregnation is most sensitive to changes in the density of the inaccessible parts in wood. Low density of inaccessible parts, as a result of large amounts of closed pores in wood, lead to very inefficient lumen impregnation. The amount of closed pores can be analysed by helium pycnometry. This study will give a guideline on lumen impregnation to have more control over the impregnation process.

INTRODUCTION

Increasing the use of wood as a renewable and low-embodied energy building and construction material as an alternative to reinforced concrete and steel is important to reduce emissions and solid waste deriving from the global construction industry (Joseph and Tretsiakova-McNally 2010). However, wood faces issues related to properties such as durability, fire resistance and dimensional stability (Rowell 2007), which requires treatments before wood flows into the construction sector. The treatment of wood through i) chemical or thermal modifications, ii) coating, and iii) impregnation is an effective way to address some of these issues (Hill 2006). In particular, 'controlled' impregnation of specific monomers inside the cell cavity (lumen), but also possibly inside the cell wall (Schneider 1995, Cabane *et al.* 2014, Keplinger *et al.* 2015), followed by polymerisation, may enhance some properties including improvements such as increased flexural rigidity (due to more solid material, i.e. 'bulking' of the wood), better durability (due to blocking of pores), improved fire resistance etc.

For controlled impregnation (and for process evaluation/control), we need to be able to assess the 'maximum potential' and the extent of impregnation 'achieved'. For wood treatments such as chemical modification or cell-wall impregnation that act on the mass part of wood, the extent of impregnation ‘achieved’ can be directly evaluated by weight percentage gain (WPG); while for lumen impregnation where the impregnant acts on the void part of wood, the ‘maximum potential’ of impregnation is determined by the void fraction (porosity) and the extent of impregnation ‘achieved’ is directly related to the pore-filling ratio (PFR) of wood rather than WPG. However, the porosity and PFR of wood samples are not as easy to obtain as WPG being collected during processing. Therefore, it is meaningful to link the porosity and PFR to easily-accessible data like WPG and density, thereby also being able to assess lumen impregnation through WPG, though indirectly.

Herein, we i) establish a simple but effective experimentally-validated relationship between WPG and apparent density for Sitka spruce, from where the PFR can be obtained; ii) analyse process-related parameters (i.e. specimen length and hydraulic pressure) that affect the extent of impregnation; iii) determine the accessibility (related to open pores) and inaccessibility (related to closed pores) of wood and how they relate to the extent of impregnation.

MODEL DESCRIPTION

The physical composition of dried wood can be simplified to a void part and solid part, as shown in Figure 1. The void part relates to the accumulation of all open pores which are accessible to impregnants. The density of the void part (ρ_A) is neglected and taken to be zero. Solid means inaccessible. Ideally, the solid part relates to the accumulation of the skeleton of the cell wall. However, if there are closed pores embedded which are inaccessible to impregnants, the solid part is then of an average property (volume and density) of both cell wall and closed pores.

(a) Simplified model for wood **(b) Model considering closed pores**

Figure 1: A simplified model for dried wood with lumen impregnation. V, ρ denote, respectively, the volume and density of void part (A), solid part (B), and filling (P). Void part relates to the accumulation of all open pores accessible to impregnants. Solid part relates to the accumulation of skeleton of cell wall including closed pores inaccessible to impregnants.

During lumen impregnation, the bulk flow of the monomer mixture fluid (filling) is transported through the interconnected voids of wood under a certain static pressure gradient (Siau 1984). The pore-filling ratio can be defined as the volume fraction of fillings in the void part:

$$\alpha = V_p/V_A * 100sfs\alpha = \frac{V_P}{V_A} \qquad (1)$$

where α % = pore-filling ratio, V_p = the volume in void part occupied by fillings, V_A = the total volume of void part.

The volume of voids and fillings (inside the wood) cannot be measured as easily as the bulk volume (from the contours of wood). However, they can be linked with weight through density:

$$V_p = M_p/\rho_p \qquad (2)$$

where M_p = the weight of fillings or weight gain, ρ_p = the density of fillings.

$$V_A = V_o - V_B = M_o/\rho_o - M_B/\rho_B \qquad (3)$$

where V_o= the bulk volume of wood including the solid part and the void part before impregnation, V_B = the volume of the solid part, ρ_o = *the apparent density of wood*, ρ_B = the density of the solid part, M_o = the bulk weight of wood before impregnation, M_B = the weight of the solid part.

As the weight or density of the void part is neglected and taken to be zero, the weight of wood before impregnation is all accounted for by the solid part, viz.:

$$M_B = M_o \qquad (4)$$

then Eqn. 3 will be:

$$V_A = V_o - V_B = M_o * (1/\rho_o - 1/\rho_B) \qquad (5)$$

and Eqn. 1 can be substituted by Eqn. 2 and 5 as:

$$\alpha = (M_p/M_o) * (1/\rho_p) / (1/\rho_o - 1/\rho_B) \qquad (6)$$

As weight percentage gain is defined as:

$$WPG = M_p/M_o * 100 \qquad (7)$$

Therefore, a relationship between WPG and apparent density of wood is derived:

$$WPG = \alpha * \rho_p * (1/\rho_o - 1/\rho_B) \qquad (8)$$

In this relationship, apparent density can be obtained by recording the bulk volume and weight of wood before impregnation; WPG can be calculated by the weight of wood before and after treatment; ρ_p depends on the filling used and usually is known or can be easily obtained from the volume and weight of the liquid.

If samples of different apparent density are treated under the same conditions, by plotting their WPG against the reciprocal of apparent density ($1/\rho_o$) and fitting a curve according to a linear model, PFR (α) may be obtained from the slope of the curve. As a by-product, the density of the solid part of the wood (ρ_B) can also be found from the interception.

It is noteworthy that there are several assumptions in this model:

(1) The filling liquid is incompressible, or ρ_p = constant;

(2) The filling only flows into the lumen, and no swelling happens to cell wall;

(3) All samples in the impregnation system are in a state of equilibrium at the end of impregnation, so that all transport processes are finished;

(4) α is independent on ρ_o and ρ_B, which means that different wood samples under the same impregnation conditions are assumed to have the same pore-filling ratio. The last two assumptions relates to porosity, permeability and the processing time of the samples. More studies are ongoing to improve the current model when considering the permeability effect.

EXPERIMENTAL

Materials

Samples of Sitka spruce (*Picea sitchensis*) were cut from flat-sawn kiln-dried timber kindly supplied by BSW Timber Ltd. The moisture content of the treated samples was around 12% determined by the oven drying method. The cross-section perpendicular to the grain direction was 10 mm * 10 mm, and the length along grain direction was normally 70 mm; however this was changed to 40 mm and 115 mm when investigating the effect of length. The actual dimensions of each sample were recorded by callipers (resolution: 0.01 mm) during processing.

Methyl methacrylate (MMA, 99%, 0.940 g/cm^3), glycidyl methacrylate (GMA, 97%, 1.070 g/cm^3), and ethylene glycol dimethacrylate (EDMA, 98%, 1.051 g/cm^3) were purchased from Sigma-Aldrich Co. LLC. The formula for the monomer mixture used in this work was MMA:GMA:EDMA (45:45:10 wt.%).

Impregnation procedures

A pressure process similar to the full-cell (Bethell) processes was used here for impregnation. Sitka spruce wood samples were vacuum-dried to constant weight at room temperature for 48 hrs. After recording the untreated weight (M_o) and dimensions (V_o), the samples were placed in a cylinder, and evacuated for 1hrs under a vacuum of less than 1 mbar. The monomer mixture were added to the cylinder while maintaining the vacuum and then a hydraulic pressure of about 1250 mbar was applied for 2 hrs. After impregnation, the monomer mixture were drained out to the recycling cylinder for reuse. The weight (M_i) and dimensions (V_i) of the treated samples were measured again after quickly wiping off the residual liquid from the surface.

Density determination

Weight and volume together determine density. Weight can be obtain quite easily once the samples, whether liquid or solid, can be put on the balance. The key issue is to measure the volume of objects, especially when the shape is irregular (which was solved by Archimedes).

Density of monomer mixture

The weight of 10 mL liquid monomer mixture was obtained by the differential weight before and after filling a 10 mL volumetric flask. Average density was calculated, by several measurements, to be 1.0054(3) g/cm^3.

Apparent density of untreated wood samples

$$\rho_o = M_o / V_o$$

As the samples we studied were cuboids their volumes were obtained by measuring the actual length of each dimension with callipers (resolution: 0.01 mm).

Density of solid part of untreated wood samples

The weight of the solid part can be regarded as the same as the weight of the bulk wood. The volume (V_B) of the solid part with irregular shape was determined using an AccuPyc 1330 helium pycnometer (MICROMERITICS). A cubic sample, with dimensions of 10 mm * 10 mm * 10 mm, was placed in the sample chamber of the pycnometer and evacuated. Then the helium gas intruded into all accessible pores in the chamber including the testing wood. As the volume of the chamber is changeable (by connecting another evacuated chamber), by recording the pressure of the helium gas under different chamber volumes, one could calculate the volume in the chamber which the helium gas could access (here it is the solid part of the wood including closed pores).

Density of cell wall

The density of the solid part may not be the true density of the cell wall if there are closed pores inaccessible to helium gas and impregnants. With the aim of obtaining the true density of the cell wall, sawdust samples were prepared by ball milling to open all closed pores to the atmosphere. The volume of sawdust was also measured by helium pycnometer. (Plötze and Niemz 2011)
The cell wall density of Sitka spruce was measured to be 1.517 g/cm^3.

RESULTS AND DISCUSSION

Relationship between WPG and reciprocal of apparent density

To validate the above model, Sitka spruce samples with the same dimensions (same length along grain direction and same cross-section) but with different density were selected for lumen impregnation. A MMA monomer mixture, which mostly fills the lumen rather than the cell wall (Zhang *et al.* 2005), was chosen with a formula of MMA:GMA:EDMA (45:45:10 wt.%) optimized from our previous work (Farina *et al.* 2014). The monomer mixture was regarded as an incompressible liquid, whose density was measured as 1.005 g/cm^3 (ρ_p). Since around 20% volume shrinkage may happen after polymerization of the MMA monomer mixture, we only used the weight gain after impregnation, but before polymerization, for the calculation of WPG. Therefore WPG is obtained by:

$$WPG = (M_i - M_{o)} / M_o * 100 \qquad (9)$$

where M_o = weight after drying but before impregnation, M_i = weight after impregnation but before polymerization.
As shown in Figure 2, WPG does have a linear relationship with the reciprocal of apparent density, which suggests that our model works well in lumen impregnation, at least for Sitka spruce.
PFR ($\alpha\%$) can be deduced from the slope of the fitting line and the density of the fillings. In our impregnation here, $\alpha\%$ was found to be 100.9 %, which suggests perfect impregnation in that all accessible voids are filled.
Although the unique slope or PFR indicates most of the samples here have the same extent of lumen impregnation, their WPG can vary from 100 to 230 due to different apparent density. Normally, the average apparent density of Sitka spruce is around 0.35 g/cm^3 ($1/\rho = 2.86$ cm^3/g), but with a considerable variation (Moore 2011). This explains why WPG is not suitable to directly describe the extent of lumen impregnation, where a bigger WPG does not mean higher pore-filling ratio.

The advantage of using WPG is that the determination of weight is easy and practical. From our model here, WPG can be kept and used to assess PFR, once the apparent density of the untreated wood is known. Timbers used in industry usually have a regular shape so that the bulk volume, as well as the apparent density, can be easily measured.

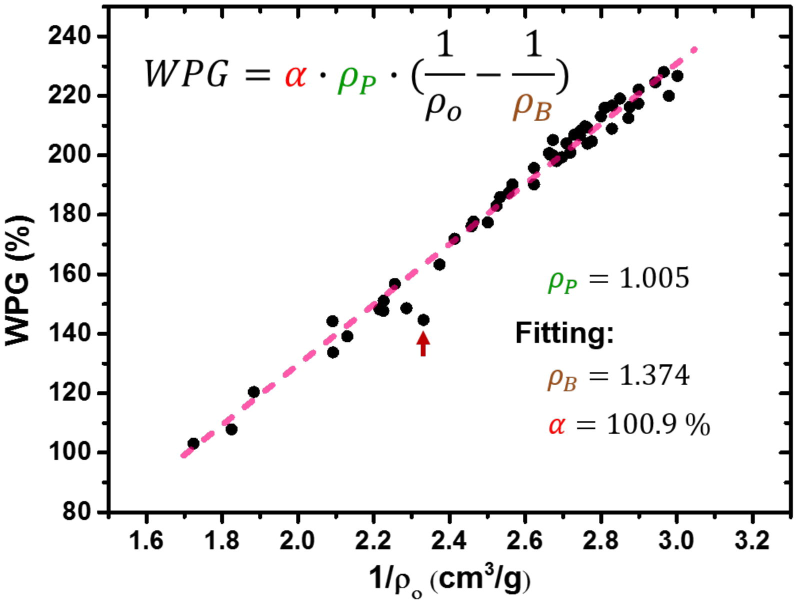

*Figure 2: Relationship between WPG and the reciprocal of apparent density. The density of MMA monomer mixture (ρ_p) is measured as 1.005 g/cm^3. Through linear fitting according to Eqn. 8, a PFR (α%) of 100.9 and the density of solid part of wood (ρ_B) of 1.374 are obtained from the slope and interception, respectively. Processing condition: Sitka Spruce, 10 mm*10 mm*70 mm (grain direction), vacuum dried for 48 hrs, vacuum (~ 1mbar) for 1 hrs, soaked for 2 hrs under 1250 mbar, filling: MMA: GMA: EDMA (45:45:10 wt.%). Note: The arrowed point in the figure was not used for fitting.*

Effect of hydraulic pressure and specimen length on lumen impregnation

Based on this evaluation method, we can study the effect of different process-related parameters on lumen impregnation.

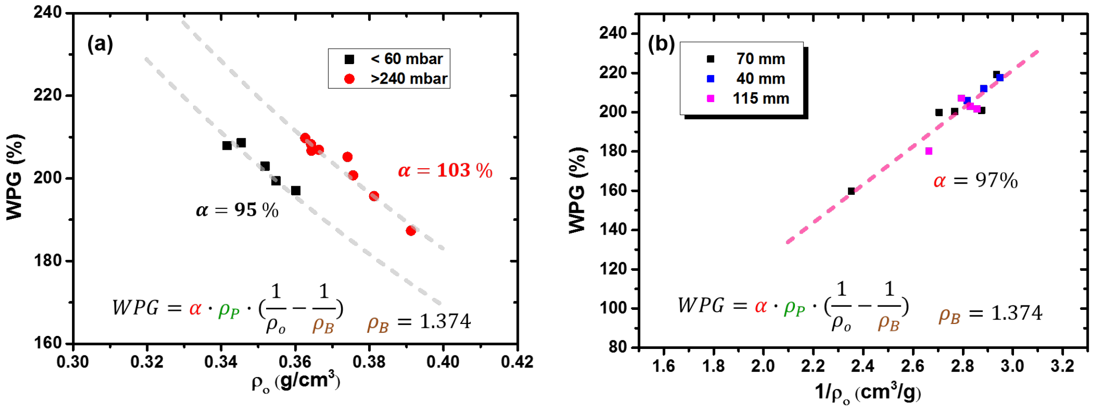

Figure 3: Effect of hydraulic pressure (a) and specimen length (b) on lumen impregnation. All PFR (α%) are obtained by using ρ_p = 1.005 g/cm^3 and ρ_B = 1.374 g/cm^3 as the fitting parameter for Eqn. 8. Pressure shown in (a) is the differential pressure against atmosphere.

As shown in Figure 3a, a hydraulic pressure of around 1240 mbar leads to a PFR of 103 %, higher than the PFR of 95 % which resulted from the lower pressure of 1060 mbar, which suggests that the extent of lumen impregnation can be controlled by hydraulic pressure.

Samples with different length along grain direction (40 mm, 70mm, and 115 mm) were treated in the same batch. As shown in Figure 3b, all samples fitted well to a unique PFR of 97 %, suggesting that the length range we studied had negligible effect on the extent of impregnation. Normally, different lengths should cause different permeability. Under the 2 hrs pressure process in our case, the variations in length may be not large enough to induce obvious changes in PFR. Samples with larger dimensions and under shorter processing times are currently under study.

Density of inaccessible part of untreated wood

The interception of the fitting curve in Figure 2 can also tell us the density of the solid part of the untreated wood, ρ_B= 1.374 g/cm^3. Ideally, the solid part should be the cell wall mainly containing 40-50% cellulose (1.56 g/cm^3), 20-35% hemicellulose (1.46-1.80 g/cm^3), and 15-35% lignin (1.33-1.38 g/cm^3) (Barnett and Jeronimidis 2009), whose density is usually reported at around 1.5 g/cm^3 (Plötze and Niemz 2011). We did determine the cell wall density of our Sitka spruce by grinding samples into sawdust, giving a value of 1.517 g/cm^3 through helium pycnometer.

The lower density obtained from the experiment indicates that the solid part, or inaccessible part defined in Figure 1a, not only includes cell wall but should also include closed pores, as illustrated in Figure 1b. If the closed pores are inaccessible to liquid impregnants, they are probably also inaccessible to gas. Therefore, we may use gas pycnometer to directly determine the density of the solid part including closed pores. As shown in Figure 4, the samples used for fitting (pink dash) do have an inaccessible density of about 1.38 g/cm^3, measured by helium pycnometer.

The Sitka spruce we studied generally had an inaccessible density of around 1.38 g/cm^3. However, timbers produced from different regions may have different ρ_B. As a suggestion, in practice, the ρ_B of representative samples can be determined before using our model to evaluate PFR.

We find that ρ_B may also depend on the anatomical structure of the samples. As shown in Figure 4, samples cut from the part near knots usually exhibits lower inaccessible density. For example, the samples just beside knots showed a density of 1.032, and resulted in almost half of the WPG compared with normal samples with the same apparent density. Moreover, it seems that the $\alpha\%$ also decreased due to the decrease of inaccessible density, as $\alpha\%$ = 92 %, ρ_B = 1.22 when fitting the samples with a density of around 1.24, as shown in Figure 4 (grey dots). We think that samples with low density or cut near knots may possess a twisted internal anatomical structure, resulting in not only more closed pores but also poorer permeability. In this case, the assumptions (3) and (4) may not be satisfied, where the PFR was not independent on ρ_B, and impregnation might need more time to achieve the equilibrium state.

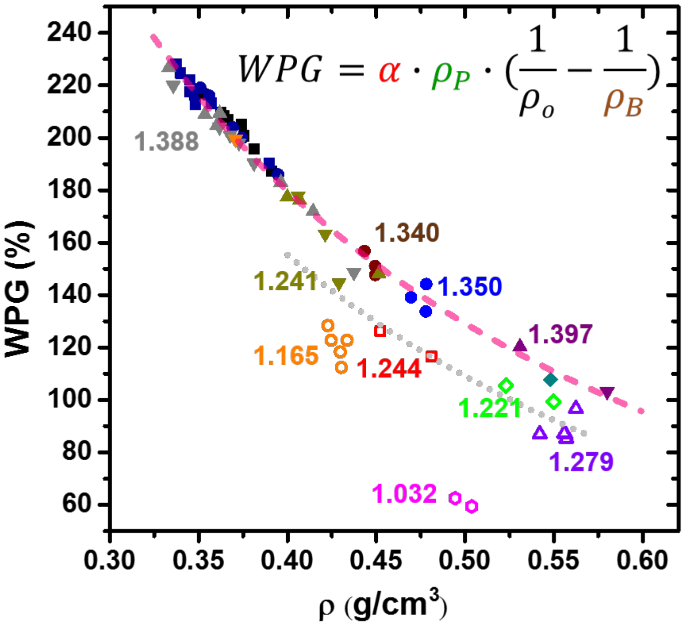

Figure 4: Effect of ρ_B on PFR. Samples with the same plot color cut from the same wood stick. All the samples were firstly cut into long wood sticks with a cross-section of 10 mm * 10 mm, then cut to required length. It is assumed that samples cut from the same stick, as shown with same color, have similar properties. Numbers in the figure are the density of untreated samples (with the same color) measured from helium pycnometer. For clear illustration, ρ_o is used as horizontal axis.

CONCLUSIONS

This study gives a guideline on lumen impregnation to have more control over the impregnation process based on process parameters (viz. product dimension and applied pressure) and sample property (viz density). We have developed a simple but effective, experimentally-validated, model to describe the relationship between WPG and apparent density, where PFR and ρ_B can be obtained from linear fitting. This therefore enables the extent of impregnation to be predicted if the apparent density of the product is measured. Impregnation is most sensitive to changes in inaccessible density, followed by changes in impregnation pressure, followed by changes in specimen length.

We note that there may be a relationship between α and ρ_B. Our future studies will investigate the permeability effect and the accessibility of the closed pores by considering removal of pits through chemical/biological (enzymatic) processes. This may also help us have more control over our impregnation process. We also plan to test our model on other types of softwood, and even hardwood. It would be interesting to also consider the effect of swelling.

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Combination of Thermal and Chemical Modifications to Improve Durability of Heat Treated Wood towards European Termites

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ABSTRACT

Even if some of the properties of thermally modified wood, like its decay resistance or dimensional stability, are improved, the overall durability of the material is insufficient to envisage utilizations in conditions where it is in direct contact with soil or termites. Previous experiments have shown that impregnation with borax associated with different vinylic monomers (aimed at polymerisation and fixation of boron) followed by thermal treatment at 220°C could be an efficient way of improving the durability of thermally modified wood. To have better insight into the potential of such combined treatments associating chemical and thermal modification, pine blocks samples were impregnated with solutions with or without polyglyglycerol methacrylate (PGMA) and different boron concentrations and thermally modified at 220°C before evaluation of the decay and termite resistance. Combined treatments using a first impregnation of borax (2 or 4% BAE) with 10% PGMA in water, followed by thermal treatment under nitrogen at 220°C permits the protection of wood against both termites and fungal decay. Such treatments appear of value in permitting the utilization of heat treated in termite infested areas. In a more interesting way, wood samples treated with a 10% aqueous solution of PGMA and subjected to thermal treatment at 220°C are also totally resistant to fungi and termites avoiding the use of any biocide. According to our results, it appears possible to envisage the utilization of thermally modified wood in areas infested with termites on the condition of associating it with a prior impregnation treatment with suitable additives. Further studies are in progress to more deeply evaluate the potential of such an approach, which could constitute an attractive alternative for wood protection in hazard class 4.

INTRODUCTION

The heat treatment of wood is an attractive alternative to improve the decay resistance and dimensional stability of wood species with low natural durability (Militz 2002, Vernois 2001, Patzelt *et al.* 2002, Esteves and Pereira 2009). However, the durability of heat treated wood is generally not sufficient for use in hazard classes, where wood is subjected to insect attack, especially in termite-infested areas (Mburu *et al.* 2007, Surini *et al.* 2012) or in ground contact in the presence of soft rot (Raberg *et al.* 2012). Moreover, the degradation of wood components and particularly of hemicelluloses, which connect cellulose and lignin in the cell wall, weakens the wood (Yildiz *et al.*

2006, Korkut *et al*. 2008, Mburu *et al.* 2008, Candelier *et al.* 2013). The future progress of thermo-modified materials will depend on developments that permit their utilization in use Classes 3 and 4 according to EN 335-2 (2007). One way to reach these objectives is to combine boron impregnation and thermo-modification. Indeed, boron compounds, such as boric acid, disodium tetraborate decahydrate (borax) or disodium octaborate tetrahydrate (DOT), are considered to be relatively safe biocides, which have proven efficacy for non-ground contact applications. These compounds have been shown to be highly effective against insects like termites and decay fungi. Borates are non volatile, colourless, odourless, non-corrosive, non-flammable and inexpensive. However, one restriction to their use in timber preservation is their natural solubility in water leading to their rapid depletion from treated wood under outdoor conditions. Several alternatives have been described to limit boron depletion (Obanda *et al.* 2008). These alternatives involve the use of water repellents or polymerizable monomers (Baysal *et al.* 2004, Kartal *et al.* 2004a, Mourant *et al*. 2009, Temiz *et al.* 2008), the formation of insoluble complexes (Kartal and Green 2003, Kartal and Imamura 2004b), the formation of protein borates (Thévenon *et al.* 1997, Thévenon *et al*. 1998, Thévenon and Pizzi 2003), the formation of organic borates with different polyols like glycol, glycerol, mono glycerides or polyvinyl alcohol (Gezer *et al.* 1999, Toussaint-Dauvergne *et al.* 2000, Mohareb *et al.* 2010), or gel formation (Mohareb *et al.* 2011, Obounou *et al.* 2013). Among these alternatives, several approaches involve the impregnation of boron with different additives intended to assure its fixation after heating. In this context, we have recently demonstrated that thermo-modification of wood samples impregnated with boron in the presence of different water soluble vinylic monomers allowed for an improvement in the resistance of boron to leaching (Salman *et al.,* 2014). The aim of this paper is to report results concerning the effects of such treatments on improvements to the durability of treated wood against different brown rot fungi and termites.

EXPERIMENTAL

Materials

Mini-blocks (15 by 5 mm in cross section by 20 mm along the grain) of Scots pine sapwood (*Pinus sylvestris L.*) were used throughout this study. Sixty replicates were used for each treatment solution. Heat treatment was performed at 220°C and half of these samples were subjected to leaching to determinate boron fixation.

Blocks impregnation

Different impregnation solutions were prepared with or without polyglyglycerol methacrylate (PGMA) and different boron concentrations. PGMA was synthesised according to a procedure already published (Soulounganga *et al.* 2004) and used at 10% concentration (w/w). Boron was tested at two Boric Acid Equivalent (BAE) concentrations (2 and 4%) using sodium tetraborate decahydrate (borax). Mini-blocks (60 replicates) were oven dried at 103°C for 48 hours and weighed (m_0). Wood samples were vacuum treated at 5 mbar for 15 min, impregnated with the treatment solutions and kept immersed for 30 min. at atmospheric pressure. Wood samples were removed from the solution and kept for 16 hours at ambient temperature, dried at 103°C for 48 hours and weighed (m_1). Weight percent gain (WPG) was calculated as follows:

$$\text{WPG (\%)} = 100 \times (m_1 - m_0)/m_0 \qquad (1)$$

where m_0 is the initial dry mass of wood samples without treatment and m_1 is the dry mass of treated wood samples.

Heat treatment

Heat treatment was performed under nitrogen in a 500 mL reactor on the different wood samples previously treated with boron, with or without additives, at 220°C for 20 hours in a Carlo Erba GC oven. The oven temperature was increased by 20°C min^{-1} from ambient to the final temperature. The accuracy of the temperature was estimated to ±1% of the set temperature. Samples were weighed after treatment and the mass change after impregnation and thermo-modification (ΔM) calculated according to the formula:

$$\Delta M\ (\%) = 100 \times (m_0 - m_2) / m_0 \qquad (2)$$

where m_0 is the initial oven dried mass of the sample before impregnation and heat treatment and m_2 the oven dried mass of the same sample after heat treatment.

Boron leaching procedure

Leaching was performed according to a procedure adapted from the European standard ENV 1250-2 (European Committee for Standardization 1994). Half of the samples (thirty replicates) were immersed in 300mL distilled water and subjected to six leaching periods of increasing duration under continuous shaking at 20°C. Water was replaced for each leaching period after 1 hour, 2 hours and 4 hours. Samples were then removed and air dried for 16 hours. Other leaching periods were conducted for 8 hours, 16 hours and 48 hours with a water change between each. After leaching, the blocks were dried at 103°C for 48 hours and weighed (m_3). Mass change after impregnation and thermo-modification and leaching (ΔM) was calculated as before using the following formula:

$$\Delta M\ (\%) = 100 \times (m_0 - m_3)/m_0 \qquad (3)$$

where m_0 is the initial dry mass of wood samples without treatment and m_3 is the dry mass of the impregnated heat treated wood samples after leaching

Decay tests

The treated specimens were tested to evaluate their resistance to fungal attack according to the guidelines specified in EN 113 (1997). The Scots pine samples were exposed to three brown rot fungi: *Coniophora puteana*, *Poria placenta* and *Gloeophyllum trabeum*. Sterile culture medium prepared from malt (40 g) and agar (20 g) in distilled water (1 L), was placed in a culture flask inoculated with a small piece of the mycelium of a freshly grown pure culture and incubated for 2 weeks at 22°C and 70% HR to allow full colonization of the medium by the mycelium. All wood samples were sterilized by autoclave at 121°C for 20 min. In each culture flask, four specimens (three treated and one control) were inserted. Virulence controls were also performed on nine specimens of Scots pine. Incubation was carried out for 16 weeks at 22°C under controlled humidity conditions of 70% RH in a climatic chamber. Once the fungal exposure was completed, the mycelium was removed and the specimens were weighed in order to evaluate their humidity at the end of the fungal exposure. The specimens were then dried at 103°C, and their final weight was recorded. The humidity at the end of the test (data not shown) as well as the weight loss of the control were determined according to EN113. Weight loss (WL) was expressed as a percentage of the initial oven-dry weight of the wood sample according to the formula:

$$WL\ (\%) = 100\times(m_{0\ \mathrm{or}\ 2\ \mathrm{or}\ 3} - m_4)/m_{0\ \mathrm{or}\ 1\ \mathrm{or}\ 2\ \mathrm{or}\ 3} \qquad (4)$$

where m_4 is the final dry mass of wood samples after fungal exposure, m_0 is the initial dry mass of wood samples without treatment corresponding to the controls, m_2 is the dry mass of the PGMA impregnated or not wood samples cured at 220°C before leaching and m_3 is the dry mass of the PGMA impregnated or not wood samples cured at 220°C after leaching.

Termite resistance tests

Termite resistance tests were evaluated using *Reticulitermes flavipes* (ex. santonensis) termites to European standard EN 117 (2005). Prior to the test, each sample was dried at 103°C in order to obtain its anhydrous initial weight (m_0, or m_1 or m_2). For each set of treatments and controls, three replicates were tested for their resistance towards *Reticulitermes flavipes* termites. Each sample was placed in a 9-cm diameter Petri dish containing 40 g of Fontainebleau sand (4 vol sand/1 vol deionized water). The samples were placed on a plastic mesh in order to avoid waterlogging. A total of 100 termite workers, two nymphs and two soldiers were then introduced onto the sand. Pine sapwood controls were tested in the same manner. The test devices were placed in a dark climatic chamber at 27°C with relative humidity > 75%. After 4 weeks, the samples were removed from the test devices. Each sample was cleaned of sand and the survival rate of the termites was calculated. The samples were dried at 103°C and their weight loss (as a % of initial weight, m_0, or m_1, or m_2) was calculated as previously.

RESULTS AND DISCUSSION

Characteristics of the different samples used for biological test are presented in Table 1.

Table 1: Characteristic of treated pine sapwood samples used for durability tests

BAE [a]	[PGMA]	WPG	ΔM		Boron content [b]	
			Before leaching	After leaching	Before Leaching	After Leaching
(%)					(kg BAE/m^3)	
0	0	-	-9.8±1.5	-	-	-
0	1	11.8±1.6	-6.7±1.6	-6.9±1.1	-	-
2	0	1.7±0.5	-8.7±1.7	-14.0±1.5	31.1	1.3
2	10	14.0±1.2	1.4±2.1	-0.5±0.7	26.9	5.7
4	0	4.6±0.6	-3.9±0.8	-15.0±1.6	54.9	1.8
4	10	16.3±2.1	6.7±2.1	4.9±1.7	59.2	7.0

[a] BAE = Boric Acid Equivalent, [b] according to Salman et al., 2014

In general, the results obtained are quite similar to those already obtained in our previous study concerning the evaluation of the different treatments on boron fixation (Salman *et al.*, 2014). Without any treatment, mass variation corresponds to the classical mass loss generally observed during thermal treatment due to thermal degradation of the wood cell wall polymers. In the presence of 10% polyglycerol methacrylate, two opposing effects are observed: on the one hand impregnation of PGMA leads to an increase in the mass of the sample, whilst on the other, thermal treatment results in the above mentioned decrease in the mass of the sample. The cumulative effects of impregnation with PGMA followed by curing at 220°C for 20 hours results in a slightly lower negative mass change than that recorded for thermal modification alone indicating a mass loss probably due to the degradation or transformation of the impregnated polymer. The impregnation of borax before thermal modification tends to slightly reduce the effect of thermal degradation reactions and consequently the mass loss caused by thermal modifications, corroborating results already described in the literature (Kartal 2006; Kartal *et al.* 2008; Kikuchi *et al.* 2007; Tomak *et al.* 2011). Similar effects were observed for treatments involving associations of polyglyglycerol methacrylate and borax, for which mass change after impregnation and thermal modification remained positive.

To evaluate the effect of the addition of PGMA on boron retention highlighted in our previous study (Salman *et al.*, 2014), leached and unleached samples were subjected to different durability tests against termites and fungi. The effects of the different treatments on wood durability are described in table 2.

Table 2: Decay and termites resistance of pine

	Resistance to fungi Weight Loss ^{a}			**Resistance to termites** ^{b}	
Treatment	*Poria placenta*	*Coniophora puteana*	*Gloeophyllum trabeum*	**Weight Loss**	**Survival rate**
	---------------------- (%) --------------------			---------- (%) ------------	
control	31.24±3.7	35.63±8.3	27.47±4.1	26.17±3.99	87
220°C	0.33 ± 0.8	0.25±0.6	0.78 ± 0.9	19.92±2.64	54
220°C and leaching	0.33 ± 0.8	1.12±1.7	0.28 ± 0.4	29.03±2.31	60
PGMA 10%, 220°C	0.11±0.1	0±0	0 ± 0	5.46±1.74	1
PGMA 10%, 220°C and leaching	0.69±0.4	0.16±0.2	0.58±0.8	5.95 ± 1.41	2
2% BAE, 220°C	2.02±1.4	0.96±1.0	1.07±0.8	3.78 ±0.31	0
2% BAE, 220°C and leaching	2.22±1.7	1.4±0.4	2.49±1.3	16.07±8.25	21
2% BAE, PGMA 10%, 220°C	1.56±0.7	0.69±0.3	1.34±1.2	2.96±0.43	0
2% BAE, PGMA 10%, 220°C and leaching	1.95± 0.5	0.53±0.7	2.99±0.9	3.45± 0.83	0
4% BAE, 220°C	1.17±1.1	0.81±0.9	0.32±0.4	3.37±1.04	0
4% BAE, 220°C and leaching	3.85±2.9	2.19±1.0	0.7±1.2	8.51±1.8	18
4% BAE, PGMA 10%, 220°C	0.7±0.2	0.55±0.8	0.07±0.2	2.81±0 .33	0
4% BAE, PGMA 10%, 220°C and leaching	2.86±1.1	2.43±1.8	3.86±0.7	2.45± 0.23	0

^{a} *average value on 9 replicates,* ^{b} *average value on 3 replicates*

Untreated pine samples are strongly degraded by the three brown rot fungi used, as well as by termites. After thermal treatment all the samples are, as expected, more resistant to fungi, while they exhibit no improvement in durability towards termites. The addition of boron allows the durability of wood to termites to be improved even after thermal treatment. However, boron fixation was not sufficient to achieve efficient protection of wood blocks after leaching. Indeed, samples impregnated with 2% BAE and subjected to thermal treatment are strongly degraded by termites after leaching. The quantity of boron retained in wood after impregnation with 4% BAE solution after leaching seems sufficient to prevent termite degradation. However, it is likely that harder leaching conditions will result in a loss of durability due to the depletion of boron. The impregnation of boron with PGMA permits an efficient fixation of boron allowing wood protection even after leaching whatever boron concentrations are utilized. The mass loss of the pine samples exposed to termites was low and practically all termites died at the end of test, while samples treated with boron without the addition of PGMA showed important mass losses and higher survival rates at the end of the test. These results are in good agreement with the quantities of boron remaining in wood measured in our previous study (Salman et al., 2014) showing a positive effect from the addition of PGMA on the fixation and retention of boron after leaching. More surprisingly, and in contrast to the heat treated samples, samples heat treated in the presence of 10% PGMA without the addition of boron also showed improved resistance to termites. This last results is of particularly interest allowing the development of a completely non "biocidal treatment" to be envisaged. This needs further investigations to evaluate the relevance of such an approach.

CONCLUSIONS

The results presented in this paper indicated clearly that boron fixation could be improved by the addition of PGMA. Combined treatments using a first impregnation of borax (2 or 4% BAE) with 10% PGMA in water, followed by thermal treatment under nitrogen at 220°C permits the protection of wood against both termites and fungal decay. Such treatments appear of value in permitting the utilization of heat treated in termite infested areas. In a more interesting way, wood samples treated with a 10% aqueous solution of PGMA and subjected to thermal treatment at 220°C are also totally resistant to fungi and termites avoiding use of any biocide. According to our results, it appears possible to envisage the utilization of thermally modified wood in areas infested with termites on the condition of associating it with a prior impregnation treatment with suitable additives. Further studies are in progress to more deeply evaluate the potential of such an approach, which could constitute an attractive alternative for wood protection in hazard class 4.

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Impact of Air Plasma Treatment at Atmospheric Pressure on Wood and Wood Extractives

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ABSTRACT

This study addresses the question of whether the extractives or the main components of wood are responsible for the alterations in surface energy after air plasma treatment. For this purpose, x-ray photoelectron spectroscopy (XPS) was carried out on untreated, microtomed, and air-plasma modified beech wood surfaces. A dielectric barrier discharge (DBD) at atmospheric pressure was used for plasma modification. The results indicate that air plasma treatment affects the O/C-ratio and surface energy characteristics of wooden surfaces by oxidative alteration and exposition of the wood main components.

INTRODUCTION

Several studies (Podgorski *et al.* 2000, Rehn *et al.* 2003, Lecoq *et al.* 2008, Odrášková *et al.* 2008, Wolkenhauer *et al.* 2008, Busnel *et al.* 2010) have shown that plasma treatment positively affects wood surface characteristics mainly by increasing the polar component of surface energy. The main components in wood are lignin, hemicellulose and cellulose, which account for approximately 95% of the wood mass, and smaller amounts of various other ingredients—so-called extractives—which can nevertheless significantly affect the surface properties (Hse and Kuo 1988, Nussbaum *et al.* 2002). Klarhöfer *et al.* (2010) demonstrated oxidation (generation of oxygenated functional groups) of lignin and reduction of cellulose (loss of hydroxyl groups, generation of C/O double bonds) as a result of plasma treatment. Additionally they showed that components of the lignin structure (e.g. coniferyl alcohol) and cellulose (glucose and cellobiose) underwent degradation when exposed to air plasma. Jamali and Evans (2011) reported a decay of wood surfaces after low-pressure H_2O-plasma treatment and revealed a higher susceptibility of cellulosic material to plasma conditions. Avramidis *et al.* (2012) demonstrated oxidation and rapid decay of pine wood extractives when exposed to atmospheric-pressure air plasma by means of surface-sensitive XPS (information depth < 10 nm). Wolkenhauer *et al.* (2009) compared aged, freshly sanded and air plasma- modified wood surfaces with respect to their surface energy. They found that a considerable increase in the polar part of the surface energy for fresh surfaces was surpassed by plasma-treated ones and attributed this observation to the removal of wood extractives from aged wood surfaces. Inari *et al.* (2011) reported data corruption in XPS-data recorded on extractive rich softwood surfaces (spruce and pine). They stated that vacuum conditions in the measurement chamber of the XPS-apparatus led to the migration of extractives to the surface. In contrast, Inari *et al.* (2006) could show a high reproducibility of XPS-data for beech wood and attributed this to its relatively low extractive content.

Aged, fresh (by microtoming), and plasma-treated beech surfaces were examined by XPS in order to demonstrate the extent to which wood extractives or wood main components contribute to surface energetic characteristics after air plasma treatment at atmospheric pressure. For this purpose, O/C-ratios were determined along with the contributions of individual carbon components of untreated and air plasma-modified beech wood surfaces.

EXPERIMENTAL

Rotary-cut European beech (*Fagus sylvatica*) veneers with the dimensions of 40 mm × 40 mm × 1.8 mm were stored in a climate chamber at 20°C and 65% relative humidity for 48 hours prior to investigation. The parameters of the DBD treatment and the measurement parameters of XPS performed on beech are described in Wascher *et al.* (2014). For XPS-analysis, small chips were cut out from the corresponding samples using a microtome blade.

RESULTS AND DISCUSSION

In preliminary studies, O/C-ratios of beech wood surfaces were determined by XPS at different time spans between air plasma treatment and XPS-analysis. Table 1 shows the results for samples in untreated and plasma-treated state.

Table 1: O/C ratio of samples determined at different time spans between plasma modification and measurement

	O/C (4h)	**O/C (24h)**
untreated	0.39	0.41
plasma-treated	0.73	0.56

The O/C-ratio for the untreated samples is very similar and amounts to 0.39 and 0.41, respectively. In contrast, the O/C-ratios of the plasma-treated specimen differ clearly, which is attributed to the different time spans between plasma treatment and XPS analysis (Avramidis 2015). A decrease in surface energy for plasma-treated surfaces with elapsing time has been reported for plasma-treated polymers (Sharma *et al.* 2007) and also for plasma-treated wood (Tang *et al.* 2012). It is known that storing freshly-sanded or cut wood surfaces alters the surface characteristics within hours (Nguyen and Johns 1979) due to the migration of extractives to the surface. Since XPS-data stems from the first 10 nm of the surface, even a short time span between treatment and measurement can led to significant errors. With this in mind, untreated (aged), microtomed (fresh), and (aged) plasma-treated beech-wood surfaces were evaluated by means of XPS, whereby measurements were executed immediately after microtoming or plasma modification (power density ≈ 5 W/cm²).

The C1s detail spectra of corresponding specimens were recorded and deconvoluted by Gaussian fits corresponding to the four bonding states of carbon occurring in wooden material. Figure 1 illustrates the carbon spectra, the corresponding deconvolution and O/C-ratio of aged, fresh, and plasma-treated beech surfaces. As can be seen, the centroid of the spectra shifted towards oxygen-bonded carbon for both the microtomed and plasma-modified samples, whereas the effect is more pronounced for the plasma-modified specimen. The surface-energy data of the polar part provided by Wolkenhauer *et al.* (2009) for aged (13 mNm^{-1}), freshly sanded (28 mNm^{-1}), and plasma-treated (30 mNm^{-1}) beech surfaces is in (qualitative) accordance with the presented O/C-ratio (n=4) derived by XPS, although no quantitative conclusions can be drawn.

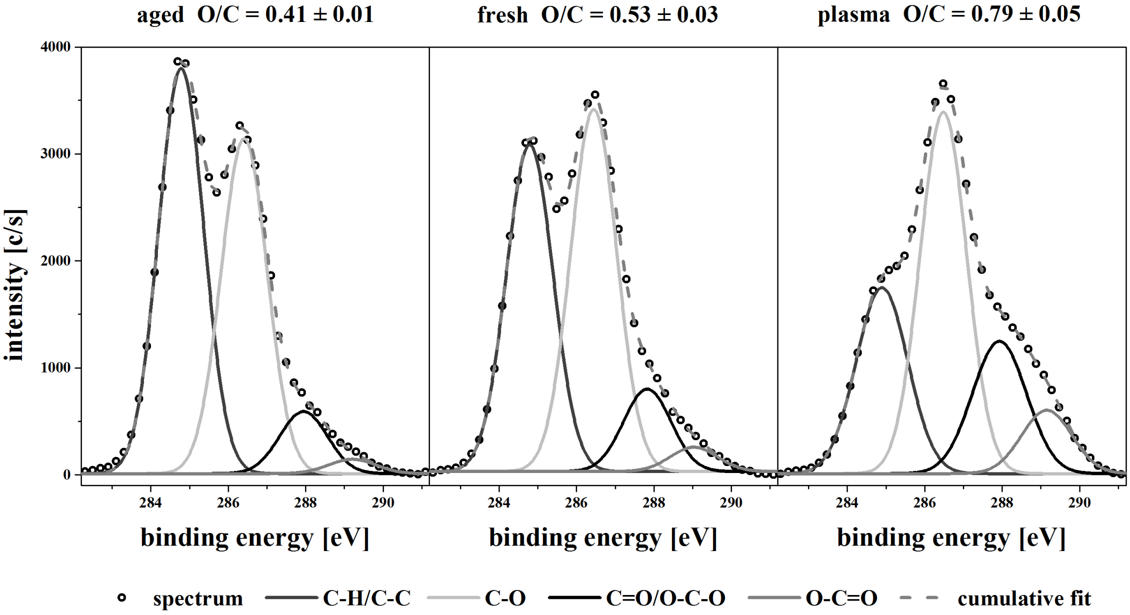

Figure 1: XPS C1s detail spectra of aged, microtomed, and air-plasma modified beech-wood surfaces (Avramidis 2015)

In order to quantify the effect, the ratios of the different carbon components per total carbon amount can be calculated. This requires the integration of the C1s spectrum and the integration of the fit function of the corresponding carbon peak. Division gives the atomic mass percent of the carbon component. Figure 2 depicts the calculated ratio of the four carbon components of the C1s spectrum. A comparison of the microtomed surfaces with the untreated/aged ones reveals a shift from C-C/C-H (C1)-bonded carbon to C-O (C2) and C=O/O-C-O (C3)-bonded carbon, whereas the O-C=O (C4)-bonded carbon peak remains nearly unaffected. In contrast, the increase in the carboxylic component is restricted to plasma modification most likely due to the generation of functional groups by reactive plasma species.

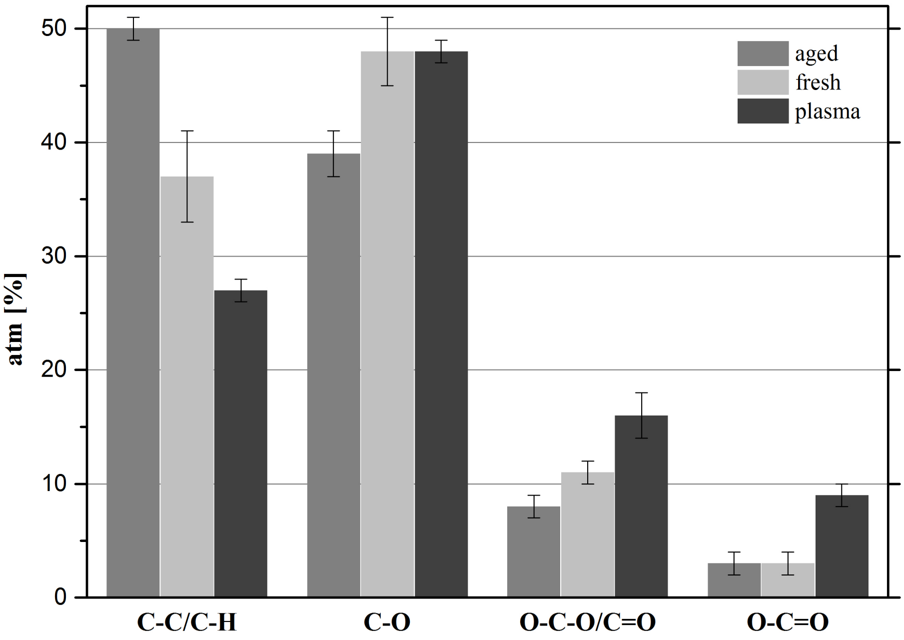

Figure 2: Calculated fracture of the four carbon components for aged, microtomed, and plasma-modified beech surfaces (n=4)

The presented XPS-data are in accordance with the findings of Klarhöfer *et al.* (2009) who reported the occurrence of the C4-peak for air plasma-treated spruce. The increase in the C2-peak and C3-peak for the plasma-treated specimens can be explained by the removal of carbon-rich contaminants (environmental contaminants and wood extractives), since microtomed surfaces show a similar increase in C2- and C3-components, whereas the increase in the C4-component (generation of e.g. carboxyl-groups) seemed to be exclusively attributed to plasma treatment.

In the following step, plasma-induced effects on wood extractives were considered for further discussion. Avramidis *et al.* (2012) demonstrated plasma-based oxidation and decomposition of wood extractives along with low impact to surface energy. One can assume that outlying short-chained environmental contaminants were removed first during plasma treatment. This was followed by the etching of non-volatile molecules with higher masses (which applies for wood extractives (Nzokou and Kamdem 2005)). Plasma-based decay/degradation of the outer extractive and/or contamination layers expose the main components of wood, which show in sum high O/C-ratios (0.68 – 0.70) (Inari *et al.* 2011). The high intrinsic O/C-ratio (due to oxygen-containing functional groups) should therefore be involved (along with the plasma-induced generation of polar functional groups) in the increased polar surface energetic behaviour.

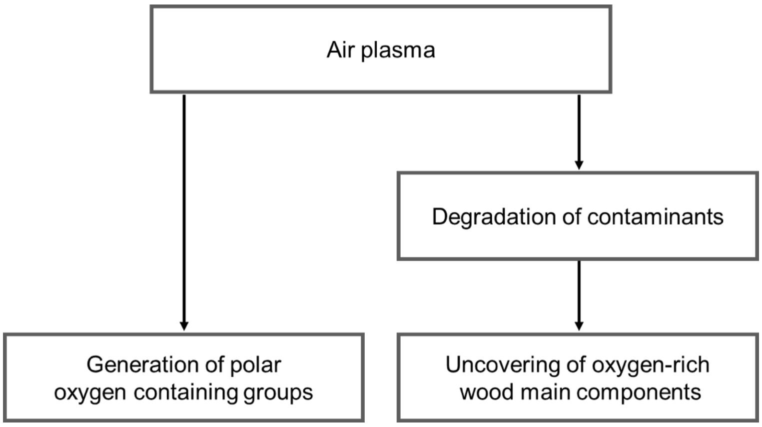

Figure 3: Two possible paths to increase the O/C-ratio and the surface energy by air plasma treatment

This means that the increase of O/C-ratio and surface energy reported by several authors can be attributed to two pathways: (1) the generation of polar functional groups by plasma-generated oxygen-species and (2) the plasma-based removal of carbon rich layers, uncovering the material beneath (see Figure 3). Both mechanisms would lead to an increased surface polarity and thus increased wetting characteristics.

CONCLUSION

It could be shown that the time span between plasma treatment and XPS-analysis can significantly influence recorded data. The XPS-data of micrcotomed and plasma-treated surfaces show a distinct chemical shift towards oxygen-bonded carbon, with a more pronounced effect for plasma-treated samples. In contrast to microtomed surfaces, the carboxylic moieties are significantly increased. The results of this study lead to the assumption that the decay of wood extractives, the exposition of main wood components, and the consequent oxidative alterations of exposed lignin and (hemi)cellulose are primarily responsible for the observed alterations in polar surface energetic behaviour.

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Bonding of Acetylated Wood

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ABSTRACT

Through modification by chemical, physical or mechanical processes, various wood properties that influence the bonding quality and workability of gluing systems can be altered. This is evident for adhesion, pressing time, curing and glue line properties. Further, the applicability of testing methods need to be evaluated for determining the bonding quality of modified woods. In this paper, laboratory test results of non-load bearing laminated acetylated products are presented. The results are evaluated and discussed in respect to the chemical composition, ultra-structure and other properties altered by the acetylation process.

INTRODUCTION

The acetylation of wood to enhance its resistance to wood decaying fungi, as well as improving its dimensional stability under varying moisture conditions, has been studied extensively over the last decade (Hill 2006, Rowell 2006, Rowell and Dickerson 2014). Accsys Technologies introduced an acetylated wood product, named Accoya® wood (www.accoya.com), into the market in 2007. It is mainly used for non-structural applications such as joinery, cladding, decking and (light) civil works (Alexander 2007, Bongers *et al*. 2009). However, encouraged by the success of the two heavy load-bearing traffic bridges constructed using Accoya® wood in Sneek in the Netherlands (Tjeerdsma and Bongers 2009, Jorissen and Lüning 2010), there is increasing interest in using acetylated wood in structural applications. Its structural properties and the introduction of a design guide have been reported by Bongers *et al.* (2014a, 2014b).

For several applications, both load bearing (e.g. glulam) as well as non-load bearing (e.g. corner joints, laminated scantlings) wood needs to be bonded and the bonding quality has a significant impact on the long-term performance of the construction.

In this paper a general outline about how the properties of wood, that may influence bonding performance, are altered due to acetylation is given. In addition, the results of an experimental study of 1) commercially laminated acetylated products and 2) recommended adhesives for the lamination of acetylated wood for non-load bearing applications, are presented and discussed. Adhesives for load bearing applications are available but not considered in the scope of this paper.

BONDING OF ACETYLATED WOOD

Due to the acetylation process various material properties are altered that may influence bonding quality (Brandon *et al*. 2006, Chandler *et al*. 2005, Frihart *et al.* 2004, Larsson *et al*. 1992, Ormstad 2007, Vick *et al*. 1993, Vick and Rowell 1990). The following properties may have an impact, depending on the adhesive system and the application process:

- Chemical bonding to the wood cell wall matrix. Acetylation replaces the hydrophobic hydroxyl groups with acetyl groups (see Figure 1). This has a direct impact on adhesives in terms of the chemical bonding to hydroxyl groups.
- The covalent bonding of the acetyl groups also impacts the surface properties; the hydrophobic acetyl groups reduce the surface energy and thereby decrease the ability of water-based adhesive to wet, flow and penetrate a bonding surface (Hill 2006, Bryne and Wålinder 2010, Moghaddam *et al.* 2015).
- By acetylation, the equilibrium moisture content is reduced significantly (typically by 3 to 5% at 20°C and 65% relative humidity (RH) for highly acetylated wood). The low amount of moisture can have an impact on bonding with one-component poly-urethane adhesive systems (Beaud *et al.* 2006). In addition, the reduced wood moisture content also has an impact on the machining of the wood and normally much smoother surfaces can be obtained.
- The swelling and shrinkage behaviour is significantly reduced by the acetylation process. Compared to untreated wood, dimensional instability is reduced by 75 to 85%. Typical tangential shrinkage from wet to ovendry conditions is 1.5% for Accoya® Radiata pine (Bongers *et al.* 2008). The high dimensionally stability has a direct influence on reducing stresses in the bond lines in delamination tests associated with water immersion and drying cycles (Hofferber *et al.* 2006).
- The liquid water uptake and subsequently drying behaviour may be changed by the acetylation process (Van Acker *et al*. 2014). This impacts on delamination tests with water immersion and drying cycles.
- During acetylation, extractives can be chemically modified and can be relocated throughout the cross-section. The extractives may have an impact on the surface properties and penetration and result in chemical reactions with adhesives.
- The presence of small amounts of acetic acid (0.3 – 1.8% m/m in ovendry wood but typically less than 1.0%) in Accoya® Radiata pine. This has an impact on the (surface) pH of the wood and its buffering capacity (Ormstad 2007). These chemical properties play an important role in the reaction and curing rates of some types of adhesives.
- Increased surface hardness. Following the acetylation of Radiata pine, increases in the average Janka hardness of 44%, 53% and 80% were found for the radial, tangential and end grain orientation respectively (Bongers *et al*. 2008).
- Changed mechanical properties (Bongers and Beckers 2003, Dreher *et al.* 1961, Larsson and Tillmann 1989).

- Increased wet strength. For several mechanical properties, a smaller reduction in wet properties compared to dry properties have been found compared to untreated wood (Bongers *et al.* 2014b). This impacts upon the failure mechanism when testing bonded acetylated wood in wet conditions.

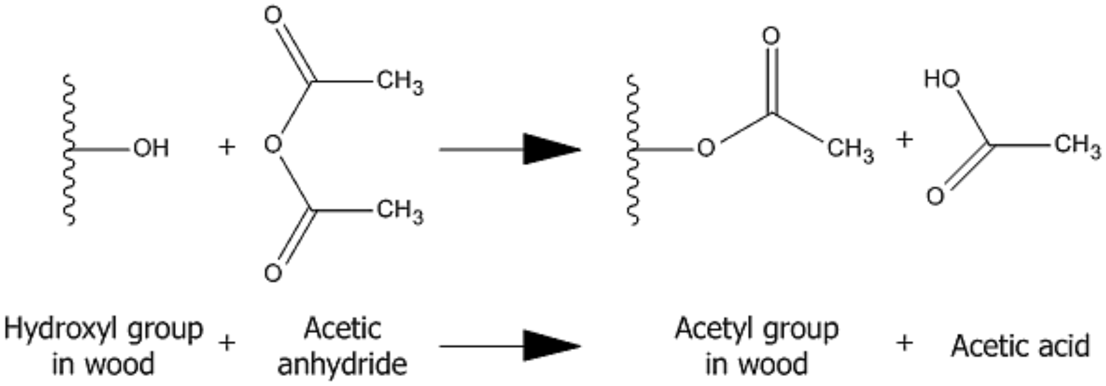

Figure 1: Schematic reaction of acetic anhydride with wood

EXPERIMENTAL

Within this research, the performance of 1) commercially laminated acetylated products (joinery scantlings of 67 x 75 mm up to 100 x 125 mm) and 2) recommended adhesive systems for acetylated wood (applied under laboratory conditions) were investigated according to non-load-bearing application standards. The adhesives used for the test fulfilled the D4 requirements of EN 204 or with type 1 of EN 301 and have been tested according to EN 205.

The recommended adhesive systems tested consisted of 1) six one-component moisture curing PURs, 2) one melamine-urea-formaldehyde resin (MUF), and 3) one PVAc for exterior applications. For each adhesive system two laminates were made with conditioned Accoya® Radiata pine and for PUR systems 1, 2, and 3, two laminates were made with untreated Radiata pine (20°C / 65% RH) as the reference. The maximum amount of adhesive recommended by the producer was applied. Since laboratory conditions were not optimal (19 °C / 40% RH) the pressing time was doubled. The laminates were put into a conditioning room (20 °C / 65% RH) for at least one week to cure. Then the laminates were cut into 12 samples of 75 x 50 x 50 mm³ by planing and not using the ends. Three samples were tested according to a block shear test and 9 samples for 3 different delamination tests, as described below.

The first delamination sequence is described in the **IFT Richtlinie HO-10/1**. After weighing, the samples were exposed to the following sequence:

- Immersing in tap water at 20 °C for 180 minutes.
- Increasing the water temperature to 60 °C and maintaining this for 180 minutes.
- Reducing the water temperature to 20 °C for 18 hours.
- Placing the samples in a conditioning room at 20 °C and 65 % RH for 72 hours.

Delamination is determined by the use of a 0.2 mm feeler gauge. The length of an open joint is measured to the nearest millimetre. To comply with the IFT standard, the maximum mean delamination is 5% and each individual sample should have a delamination less than 10%.

The second delamination test applied is described in **BRL 2902**. A 50 mm long laminated sample is subjected to the following sequence:

- 4 hours immersion in boiling water
- 20 hours drying in an oven at 65 °C

The percentage of open glue line after the test may not exceed a mean of 5% delamination for all samples and 10% per individual sample.

The last delamination test was carried out according to **CEN/TS 13307-2**. After weighing, the samples are treated as follows:

- Immersion in tap water at 20 °C for 16 hours.
- Drying in a ventilated chamber with a temperature of 50 °C (±2) and 60 % (±5) RH for 24 hours.
- Cooling in a conditioning chamber at 20 °C (±2) and 65 % (±5) RH for 1 to 2 hours. The last step was extended because full drying should be achieved.

After the test the samples were evaluated according to the standard that applies a statistical evaluation of the recorded open joint lines in relation to the wood density.
All profiles were tested in both dry and wet condition according to the **block shear test** described in CEN/TS 13307-2. The shear strength of an adhesive is deemed acceptable if the coefficient of variation in the shear strength of the un-preconditioned set is below 15% and, additionally, it should meet the criteria of the ratio between the preconditioned versus un-preconditioned sample set in relation to sample density. After the block shear test, the glue lines were visually evaluated for the amount of wood failure. According to CEN/TS 13307-2, the wood failure is acceptable if the mean wood failure of a set is above 90% and wood failure in every individual glue line is above 75%.

RESULTS

Performance of laminated acetylated products

In Table 1 a summary (failed/passed) of the test results is given for the commercially laminated acetylated products. All the products were bonded with PUR adhesives. The two Accoya®- Accoya® laminated products passed all tests. The Accoya® Radiata pine with Scots pine (*Pinus sylvestris*) laminate passed all delamination tests except for the amount of wood failure.

Table 1: Summary of results of the commercially laminated acetylated products (√ indicates passing the test, X means failed).

Scantling	Bond line	BRL 2902	IFT	CEN/TS		
				Delam.	Shear strength	Wood failure
1	Acc-Acc	√	√	√	√	√
2	Acc-Acc	√	√	√	√	√
3	Acc-Pine	√	√	√	√	X
	Pine-Pine	√	√	√	√	√

Performance of recommended adhesives

A summary of the test results (failed/passed) for the different recommended adhesive systems for acetylated wood is given in Table 2. Only one (out of the 12) laminated acetylated Radiata pine samples bonded with PUR did not comply with the requirements set out in the BRL 2902 delamination test. All other PUR bonded samples complied with the standards, except for the criteria set for wood failure (mean delamination of >90% defined in CEN/TS 13307-2). The other adhesives, PVAc and MUF, showed higher variability in their performances with acetylated Radiata pine.

Table 2: Summary of results of adhesives recommended for acetylated wood (√ indicates passing the test, X means failed, X / √ indicates one of the samples failed and one passed).

Adhesive producer	**Adhesive**	**BRL 2902**	**IFT**	**CEN/TS**		
				Delam.	**Shear strength**	**Wood failure**
1	PUR	√	√	√	√	X / √
2	PUR	√	√	√	√	X / √
3	PUR	√	√	√	√	X / √
2	PUR	√	√	√	√	X / √
4	PUR	√	√	√	√	X
5	PUR	X / √	√	√	√	X / √
6	MUF	X	√	√	√	X
7	PVAc D4	X	X	√	√	X

Table 3 summarises the results of the delamination test according to BRL 2902 and the block shear test in wet and dry conditions for untreated and acetylated Radiata pine glued with 3 PUR systems. Only 1 sample of untreated Radiata pine showed a small delamination in the severe BRL 2902 test. Overall the dry shear strength of the acetylated wood was slightly higher compared to the untreated Radiata pine. Much more pronounced was the higher wet shear strength of the acetylated samples. Wood failures are similar for the untreated and acetylated Radiata pine.

Table 3: Average delaminating (BRL 2902) and dry and wet shear strength of untreated and Accoya® Radiata pine glued with 3 PUR systems (minimum and maximum values are given in brackets)

Adhesive producer	**treatment**	**BRL 2902 [%]**	**Dry**		**Wet**	
			Shear strength [N/mm²]	**Wood failure [%]**	**Shear strength [N/mm²]**	**Wood failure [%]**
1	acetylated	0	13.4 (10.2- 18.8)	85 (69- 100)	11.7 (10.6-12.9)	20 (1-35)
	untreated	0	11.4 (10.2 -14.7)	78 (38-100)	4.0 (3.0-4.8)	8 (0-25)
2	acetylated	0	13.8 (11.1-19.3)	84 (78-100)	10.1 (8.0-11.0)	3 (0-8)
	untreated	0	11.9 (10.3-17.8)	89 (72-100)	4.3 (3.5-5.1)	5 (0-20)
3	acetylated	0	11.1 (7.9-18.0)	80 (72-100)	8.7 (6.9-10.3)	11 (0-21)
	untreated	0.1 (0-2)	11.4 (10.7-14.8)	87 (72-100)	3.9 (3.3-4.5)	1 (0-6)

Microscopic investigations

Initial fluorescence microscopic studies were done on a small number of PUR laminated untreated and acetylated Radiata pine samples. No particular differences were seen between the glue lines of the untreated and acetylated wood based on the limited amount of samples and with only 1 PUR system.

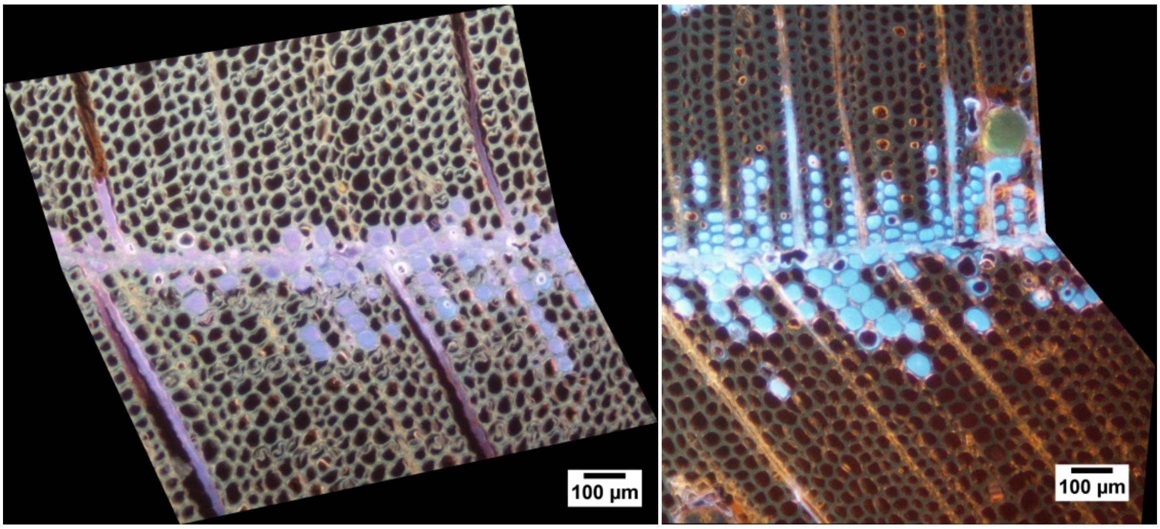

Figure 4: Microscopic image of PUR bonded Accoya® (left) and untreated Radiata pine (right).

DISCUSSIONS

Overall, the commercially laminated acetylated products (glued with PUR) and the recommended PUR adhesives performed very well in the different delamination tests. Even with the most severe weathering (exposure to boiling water for several hours followed by drying) of BRL 2902 the percentage delamination was low, meeting the requirements of the standard. The high dimensionally stability of acetylated wood has a direct influence on reducing stresses in bond lines during delamination tests associated with water immersion and drying cycles (Hofferber *et al.* 2006). Shear strength performance is also good for the PUR adhesives. Compared to untreated Radiata pine, the wet shear strength in particular was much higher for acetylated wood. As a results of acetylation, it is known that several mechanical properties are reduced to a lesser extent in wet conditions compared to untreated wood (Bongers *et al*. 2014b, Hofferber *et al*. 2006). The percentage of wood failure, however, for several untreated and acetylated samples was below the requirements of CEN/TS 13307-2 in dry conditions. In wet the condition the percentage wood failure was much lower for both acetylated and untreated wood. In the microscopic study no remarkable difference was found in the penetration of adhesive into the untreated and acetylated wood. In general, the wood failure of one-component moisture curing PUR in the wet state has been reported to be low (Kläusler 2014). For acetylated wood it is questionable whether the percentage wood failure is important as long as high shear strength values are found. Additionally, lower percentages of wood failure were found with the laminates produced at laboratory scale in this research, which is in contrast with the values found for the commercially laminated acetylated products. The commercial products all met the requirements of the standard. This illustrates the importance of the bonding process and production control. Open and closed times, the mixing of two component adhesives, and the application method (manual versus industrial) are typically parameters that may impact upon the results for laboratory tests versus commercial production.

The lower performance of PVAc is partly in contrast with other experiments by Accsys Technologies, adhesive manufacturers, gluing companies and third party notified bodies. Compared to bonding with PUR the bonding process and production control might be more critical for the PVAc adhesives.

CONCLUSIONS

Through acetylation various properties are altered that can influence the bonding quality of gluing systems. In this study it has been shown that the lamination of acetylated wood for non-load bearing application gives good performance with PUR adhesives exposed to severe delaminating test cycles, even with exposure to boiling water for several hours followed by drying. The shear strength values of acetylated wood under dry conditions are at least comparable with those found for untreated Radiata pine. Under wet conditions a reduction of only 13-27% was found for acetylated wood whereas the shear strength of untreated Radiata pine were reduced by approx. 65%. The percentage wood failure of several laboratory produced untreated and acetylated samples was beneath the requirements of CEN/TS 13307-2 in dry conditions. This conflicts with the promising results found in commercially acetylated laminated products (PUR adhesive) and illustrates the importance of the bonding process and production control.

The laminates bonded with PVAc or MUF adhesives showed poor performance in the delamination tests compared to samples acetylated Radiata pine glued with PUR. The lower performance of PVAc is in contrast with other experiments. Compared to bonding with PUR the bonding process and production control might be more critical for the PVAc adhesives.

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Accoya® and Tricoya® for Use in Innovative Joinery

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Keywords: Accoya®, Tricoya®, acetylated wood, coatings, durability, joinery, stability

ABSTRACT

The wood modification technique of acetylation, which is commercially available under the brand names Accoya® for solid wood and Medite Tricoya Extreme® for MDF, offer new levels of durability, stability and uniformity to wooden joinery manufacturing and maintenance. Both acetylated products are now widely used in such applications across Europe, based on two major approaches. The first is the substitution of all wood-based components by Accoya or Tricoya, thus obtaining a general improvement in the maintenance performance of the existing joinery product. The second is a more disruptive approach by which new joinery products and concepts, whose design and relative market position is based on increased levels of performance. This paper provides an overview of the Accoya and Tricoya material properties relevant to joinery design and service life. Further, it will focus on case studies from European joinery companies who have implemented, designed and technically positioned the products in the market so as to maximize the performance and therefore end user benefit.

INTRODUCTION

Acetylation

The physical properties of any material are determined by its chemical structure and matrix. Wood contains an abundance of hydroxyl groups (OH-groups). These adsorb and release water according to changes in the climatic conditions to which the wood is exposed. This is the main reason why wood swells and shrinks. It is also believed that the digestion of wood by enzymes initiates at the hydroxyl sites – which is one of the principal reasons why wood is prone to decay.

Acetylation is a non-toxic process which increases the number of naturally occurring hydrophobic acetyl groups in the wood cells. This involves impregnating the wood with acetic anhydride, which reacts with the hydroxyl groups in the cell walls and exchanging them for acetyl groups. Due to the reaction, acetic acid is produced as a by-product (see Figure 1). When the hydroxyl group is changed into an acetyl group, water penetrating the wood cell is not able to bind itself anymore, rendering the wood more dimensionally stable and, because it is no longer digestible, extremely durable. A comprehensive background of acetylation and its properties is given by Hill (2006) and Rowell (2006).

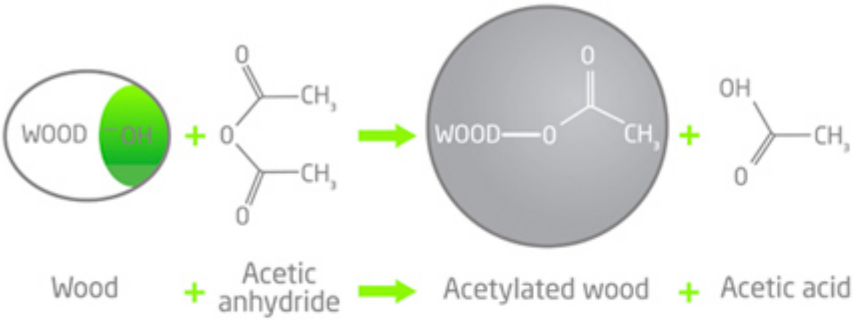

Figure 1: Acetylation of wood

Accoya®

For the first commercial production of acetylated wood in 2007, Accsys Technologies utilized the acetylation technology on radiata pine (*Pinus radiata*). This is sold under the brand name Accoya® wood and has been used for many applications worldwide, amongst which are windows, doors, cladding and decking (Alexander 2007, Bongers *et al.* 2009). Other wood species, treated according to the same principles, are under investigation (Bongers *et al.* 2008, Bollmus *et al*. 2015).

Tricoya®

Many of the benefits observed in solid acetylated wood, including enhanced dimensional stability, durability and fungal resistance also hold true for Tricoya® (Suttie *et al*. 2015). Tricoya® has been produced by Medite and has been distributed primarily in Europe since late 2011. It is made using a high performance exterior grade and formaldehyde free resin, making the product not only exceed EU E1 but also CARB2 compliant. Medite Tricoya® Extreme has been demonstrated, even in challenging weather conditions, to be suitable in situations and applications where normal MDF panels are not (Suttie 2011).

PROPERTIES AND PERFORMANCE

Any joinery product has to comply with local laws and building regulations. According to national or European building guidelines, like the EN 14351, many tests are obligatory for the end product. This involves, for example, resistance to wind load, water tightness, burglary resistance, operational force, etc. No direct requirements are given for the wood properties, although various performance obligations for the joinery product have a strong link with the properties of the raw material.

Table 1 shows the different requirements and a comparison of the properties of Accoya and Tricoya.

Table 1: Properties of Accoya and Tricoya

Property (Ac/Tric)	**Requirement**	**Accoya**	**Tricoya**
Density (kg/m³) ISO 3131 / EN 323	None for standard joinery	512	700 +/-30 based on 18mm board thickness
Durability class EN 335	DC 1, 2 or 3, depending on situation/application	DC 1	DC 1
Dimensional stability/swell ovendry to fully wet (%) WVS-SHR-047 EN 318	The higher the stability, the better. The lower the swell, the better.	Radial 0,8 Tangential 1,5	Linear: 0,1
Surface hardness, Janka (N) ASTM D143	As high as possible, especially for door thresholds	Tangential 4100	Not tested
Bending strength (N/mm²) EN 408 / EN 310	The higher the better to produce large sections	39	20 – 30, depending on panel thickness
Thermal conductivity (W/(mK) EN 12664	As low as possible	0,12	0,0949 based on 18mm board thickness

CASE STUDIES ACCOYA

Standard window design

The simplest way to fit Accoya into a standard window design is to fully replace all wood components in the construction. The end user will immediately benefit from the advantages in dimensional stability and durability. Many large coating manufacturers extended their warranty schemes up to 15 years for opaque, film forming coatings on Accoya joinery. These coatings have to be industrially applied, are relatively standard and do not have an effect on the application process.

Figure 2: Accoya in a standard English sash window design

When the customer wants to retain standard joinery details, there is another option. Apart from replacing all components with Accoya it is also possible to only replace the high risk zones with a more durable and stable wood. Before tropical hardwood emerged on the market, it was not uncommon that softwood was combined with a threshold of oak. As the highest amount of wood repair, and therefore cost of failure is always within the bottom of the element, the ‘old’ system is quite easily applicable for the beads, bottom sill and/or threshold. This minor change is very likely to extend the operational life of the full element. Some of these items, such as beads, can be produced from both Accoya and Tricoya, in line with the window company’s preference. One aspect to keep in mind when wood species of different dimensional stabilities are combined is that the glue connections have to remain intact, preventing water ingress in the vertical parts. This can either be done by very flexible glue lines or by adding more dowels to a joint, making it more rigid.

Face laminated

A different way to enhance the properties of the most demanding areas of wooden joinery is by laminating a 3 layer combination with Accoya solely on the exterior side of the element. The two lamellas on the interior side can be made from a cheap, low durability species. The impact on the total cost of the element of this so-called face-laminated material is hereby reduced, and the use of stainless steel or other corrosion resistant coated hardware is not always necessary. All details remain equal and maintenance benefits are the same compared to a solid Accoya element.

Figure 3: Accoya face laminated with 2 lamella’s of spruce

This design is especially suited to renovation as the interior side of the element is not exposed to high humidity. With regard to stability, a combination of Accoya with spruce is more favorable than with pine as the former behaves slightly better in response to moisture changes. Also other combinations with more decorative wood species such as oak, cherry or walnut on the interior side are possible. In most cases such decorative joinery a translucent coating on the interior and an opaque one on the exterior.

Howard N. (2015) visually analyzed a 30 month old window with translucent coating based on the principle of face-lamination. The element was installed in the BRE window joinery test building in the UK. He reported the conclusions listed in Table 2.

Table 2: Conclusions

General condition	Appearance excellent
Joint condition	Excellent, joints tight, coating intact, no evidence of movement or opening
Bead condition	Excellent
Coating condition	Excellent, bright, no signs of deteriorations or discolouration
Operation	Movement of opening lights was easy
Overall performance rating	Excellent

Figure 4: Accoya face-laminated windows, 30 months old on test at the controlled interior climate window exposure site, BRE, UK

Optimizing of specific details

By optimizing specific details, using the modified properties of Accoya, new element designs with improved properties are possible. A cooperation of Dutch joineries have designed an element that only needs its first maintenance after 15 years instead of after 6 years for tropical hardwoods. Moreover, there are even manufacturers that warrant a second maintenance-free period of 15 years after the first maintenance on-site. The main amendment compared to regular joinery is an increase in radius on all sharp edges to achieve optimal coating coverage. Rounding the edge with a 3 mm radius is often standard, although an even bigger radius is more beneficial for coating performance. It is also important that all coating layers and also the placement of the glass is done industrially. Apart from that all non-wood components have extended their maintenance scheme as well.

A further advantage of coating longevity relates to the bottom beads of windows and large sills. Bottom beads on high performance windows have commonly been produced from aluminium rather than wood to avoid early failure. Accoya has the performance to regain this bottom bead application for wood. Further, protruding sills are often required for joinery used in refurbishment projects to fit the design character of the building. Wide sills are frequently excluded from coating warranties, were with Accoya wide sills can be included in the warranty.

Uncoated joinery

Accoya wood does not necessarily have to be coated to maintain its durability and dimensional stability. A standard Dutch joinery design of 67 mm thickness in solid Accoya has been used for a multi-story building in Amsterdam (NL), constructed in 2010. There are a number of critical steps during the building process: 1) the elements have to be covered during storage to prevent large water uptake, 2) the building should already be relatively dry when the elements are mounted and 3) ventilation should be sufficient in order to prevent any surface mould on the interior side. The most practical solution would be to use temporary frames and apply the final frame in the last step of the building phase as the building is dry.

In monitoring this project of over 200 windows, predominantly, moisture transport from exterior to interior does not take place. Of course the outer zone of the wood takes up moisture during rain or high relative humidity. The surface is susceptible to surface mould on the exterior side, although this is only an aesthetic issue. This becomes less prominent when the wood greys and surface moulds can of course be cleaned off.

Figure 5: Uncoated Accoya joinery, Apartment building Amsterdam, The Netherlands

Use in repair work

Painters regularly do small repair works on existing elements on-site by using epoxy wood repair materials or exchange the lower, exterior glazing bead, which is often the weakest link in a wood element. The use of Accoya as replacement parts increases the maintenance period.

Figure 6: Typical on-site repair work of the 'weak' parts

CASE STUDIES TRICOYA

Tricoya is mainly appreciated for its combined technical properties, homogeneity, practical aspects such as large format (panels up to 1.2 x 4.8 m), ease of processing with CNC-equipment and a thickness range from 6 to 18 mm.

Tricoya exterior door skins (facing)

Just as with Accoya, the improved dimensional stability of Tricoya leads to increased coating performance compared to regular door facings like exterior HDF or Okoumé (*Aucoumea klaineana*) plywood. Further, this performance does not suffer in the same way in Tricoya as it does with other wood panel skins if the protective coating layer is compromised through damage at installation or in service. Many large coating manufacturers recommend their standard coatings, which do not have a large effect on the application process but can lead to up to 15 years of no re-coat warranty on Tricoya skin exterior doors. Dutch door producers have calculated that the break-even point for the higher cost price is between 5 to 8 years and most likely leads to high savings in the total cost of ownership. As the product is available in relatively thin sheets, the amount of material to be used is rather limited.

Figure 7: Typical build-up of an engineered door with Tricoya only on the two faces

Grooved panels in a solid wooden door/frame

Wood based panels, including exterior plywood, are often mounted in a solid, wooden stile and rail doors and fixed with adhesives/sealants into the frame. When the solid door is made of Accoya, Tricoya is recommended in order to have the same maintenance cycle on all elements. Secondly, plywood grooved panels are not very dimensional stable and can cause issues on the adhesives and sealant especially in larger sizes. Grooves are vulnerable to water ingress and have caused many problems in the past. European door producers have seen a significant reduction in failure costs since the introduction of Tricoya in these door types.

Glazing beads

Heritage joinery for new buildings or renovations often requires complex glazing bar arrangements. Producing this from solid wood is particularly time consuming, and even then subject to failure due to dimensional stability issues. These complex sections are ideally suited for a panel, offering the required technical properties, robustness to damage and fit with CNC processing. Tricoya has developed a substantial market in this application.

Figure 8: Tricoya complex glazing beads instead of solid wood

Complex window shapes

Laminating Tricoya into thicker dimensions and subsequently CNC profiling it to form joinery elements provides a new solution for complex window types such as a circular pivot type. In this case, both cost savings, reduced workshop skill and improved performance can be achieved.

Figure 9: Tricoya complex circular joinery

CONCLUSIONS

The material properties of Accoya® solid wood and Medite Tricoya Extreme® wood based panel product make it very suitable for joinery. High dimensionally stability, extended coating performance and increased durability open the opportunity to think beyond the normal scope of joinery applications and design. A series of case examples have been shown in this paper that illustrate that this opportunity is now being taken and is likely to be extended further.

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SESSION FIVE

Thermal Modification

Effect of Temperature and Steam Pressure during the Thermal Modification Process

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Keywords: thermally modified wood, water vapour pressure, mass loss, soluble degradation products, acidity

ABSTRACT

The impact of the process conditions during thermal modification in a high-pressure reactor system on wood degradation was studied. European beech was thermally modified under different process conditions by varying peak temperature (150-180 °C), peak duration (1-6 h) and maximum pressure (0.14-0.79 MPa), while aiming at a constant relative humidity. Wood mass loss during the process, as a marker for thermal degradation, was found to be strongly determined by the applied maximum pressure, rather than by the peak temperature. Increasing the water vapour pressure prevented water, organic acids and other degradation products from being emitted from the wood. Increasing the peak temperature suppressed this effect. Accelerated degradation at elevated pressure can thus be assigned to softening of wood polymers in the presence of water and the catalytic effects of the accumulated organic acids on carbohydrate degradation. Thermal modification at elevated pressure might offer an effective alternative to modification at atmospheric pressure. However, high quantities of water-soluble compounds in the final product might have to be considered depending on the later application.

INTRODUCTION

The thermal modification of wood to improve biological durability and dimensional stability has been extensively studied and has led to many processes technologies that have been commercially implemented during the past decades (Militz and Altgen 2014). Although in Europe huge quantities of thermally modified wood are produced in open reactor systems using superheated steam at atmospheric pressure (e.g. ThermoWood®), some recent process technologies are based on applying elevated water vapour pressure in closed reactor systems (Willems 2009).

Although a broad range of parameters can affect thermal wood modification, wood degradation and treatment intensity in open reactor systems with superheated steam at atmospheric pressure are predominantly determined by peak temperature and duration (Zaman *et al*. 2000, Welzbacher *et al*. 2007). In such reactor systems, organic compounds become largely volatile and are emitted (Hofmann *et al*. 2013), while the relative humidity decreases considerably at elevated temperatures. This low relative humidity necessitates the thermal modification of wood in an oven-dry state.

Compared to open systems, wood degradation in closed reactor systems is much faster (Stamm 1956, Burmester 1973, Borrega and Kärenlampi 2008, Rautkari and Hill 2014), indicating that additional process parameters play a major role. In contrast to open systems, the oven-dry state of the wood can be avoided in closed reactor systems by applying a sufficiently high water vapour pressure (Lenth and Kamke 2001, Ishikawa *et* *al*. 2004). However, in closed systems, the parameters of temperature, water vapour pressure and relative humidity are interdependent, which hinders the evaluation of their individual impact on wood degradation. In this study, a closed reactor system as described by Willems (2009) was used to perform thermal modification processes. This reactor system is based on controlling the water temperature independently from the temperature in the vessel, thus enabling the individual adjustment of vessel temperature and water vapour pressure throughout the process nearly up to saturated water vapour conditions.

This study evaluates process parameters that determine wood's thermal degradation in a closed reactor system. European beech wood was thermally modified at different temperatures, durations and water vapour pressures, whilst aiming at a constant relative humidity during the whole process. The degree of degradation was quantified by recording the mass loss of the wood caused by the modification process. Additionally, the moisture content of the wood was measured and soluble degradation products within the wood were analyzed.

MATERIAL AND METHODS

Material

European beech (*Fagus sylvatica* L.) wood material that originated from one log and that was conventionally kiln-dried to 11-13 % moisture content was used. Slats with dimensions of 35×65×800 mm³ and an average density of 0.63 g/cm² were prepared, while avoiding juvenile wood, major defects and large knots, as well as red heartwood. Each process run was performed with eight slats.

Thermal modification

Thermal modification processes were performed in a laboratory-scale treatment reactor, based on the technology described by Willems (2009). The treatment schedule consisted of four steps: (1) a 50 min holding step at 50 °C in a pre-vacuum; (2) a temperature increase at 12 °C/h; (3) a holding step at set point peak temperature, peak duration and maximum pressure; (4) a temperature decrease at 20 °C/h to 65 °C. The wood temperature was not recorded during the process. The pressure was adjusted by increasing the water temperature in the external water reservoir and the release of excess pressure through the gas washer using exhaust valves. During the process, the pressure control was aimed at keeping the relative humidity constant. Relative humidity, RH [%], was defined as described below (Eqn. 1)

$$RH = (P_{steam}/P_{sat}(T)) \times 100, \qquad (1)$$

where P_{steam} is the water vapor pressure, WVP, and $P_{sat}(T)$ is the temperature dependent saturated WVP. Since the WVP could not be determined directly, a pre-vacuum (< 0.014 MPa) was applied and the total pressure was used for calculation of RH. Since this is only valid under the assumption of pure steam conditions, the precise control of RH was not possible. At the end of the process, excess pressure below 0.1 MPa was not released.

During the high-temperature holding stage in step (3), peak temperature (150 - 180 °C), peak duration (1, 3 or 6 h) and the maximum pressure (0.14 – 0.79 MPa) were varied, resulting in 20 process runs with different process conditions.

Methods

Mass loss was determined by recording the weight of the slats before and after the process, as well as by measuring the respective moisture content on small samples that were taken from each slat. Moisture content, the dry weight of the slats and the mass loss of the slats during the process were calculated as described by Metsä-Kortelainen *et al.* (2006).

Material from each slat as well as from unmodified references was milled and mixed in a cutting mill and used for chemical analysis. Hot water extraction was carried out in duplicate per variety in a Soxhlet apparatus using 3 g dry wood particles and 200 ml of deionized water. The percentage of water soluble components, WSC [%], was calculated as described below (Eqn. 2).

$$\mathrm{WSC} = ((w_0 - w_1)/w_0) \times 100, \qquad (2)$$

where w_0 is the dry weight of the wood before extraction [g] and w_1 is the dry weight of the wood after extraction [g]. WSC was subtracted from the dry weight of each slat to calculate the corrected dry weight, w_c [g] as described as follows (Eqn. 3).

$$w_c = w_{dry} - ((w_{dry} \times \mathrm{WSC})/100), \qquad (3)$$

where w_{dry} is the dry weight of the slat [g]. Finally, the corrected mass loss during the process, ML_c [%], was calculated as described below (Eqn. 4).

$$ML_c = ((w_2 - w_3)/w_2) \times 100, \qquad (4)$$

where w_2 is the corrected dry weight of the slat before the process [g] and w_3 is the corrected dry weight of the slat after the process [g].

For determination of acidity, 2.5 g dry wood particles and 30 ml of deionized water were placed on a flatbed horizontal shaker at room temperature for 24 h. The extracts were filtrated and the particles were washed with deionized water to a final volume of 100 ml. Acidity was measured by titration using 0.01 M sodium hydroxide solution. The amount of sodium hydroxide required to reach the neutralization point was determined from the titration curve. This amount was used as a marker for the acidity of the wood in mmol NaOH equivalents per 100 g dry wood [mmol/100 g dw.]. Measurements were done in duplicate.

RESULTS AND DISCUSSION

As a result of the high-temperature and high-pressure regimes in the treatment reactor, changes in the wood can only be evaluated after the process. Figure 1 A shows the dependence of mass loss during the process on the maximum pressure. Both mass loss and corrected mass loss increase linearly with the maximum pressure, irrespective of the peak temperature. A similar observation was made by Willems *et al.* (2015) for Norway spruce. It is thus concluded that the thermal degradation of wood that takes place in the closed reactor system can be best described by the applied pressure, rather than by temperature. However, mass loss based on dry wood does not consider degradation products that remain within the wood, and might thus underestimate the degree of degradation that has taken place. By subtracting the percentage of water soluble compounds (WSC) from the mass of the slats before and after the process to calculate the corrected mass loss, the slope of the regression curve increases and a slightly better fit is achieved. Presumably the degradation products of cell wall carbohydrates, which are gasified when performing thermal modification processes under (sub-) atmospheric pressure, accumulate within the wood at elevated pressure. Thus, WSC in the wood must be considered when using wood mass loss as a marker for thermal degradation and treatment intensity for wood treated at elevated pressure, as previously stated by Obataya *et al*. (2002). Furthermore, high WSC in wood treated at elevated pressure might have adverse effects during its later application, e.g. in terms of VOC emissions, discoloration of coating systems, or mould growth.

From Figure 1 B, it becomes obvious that the dependence of the corrected mass loss from the applied peak duration can be described well by linear functions. The y-intercept can be considered as the mass loss that takes place outside the high-temperature holding stage, during heating up and cooling down. It considerably increases with the applied pressure. As shown by Willems *et al*. (2015), the slope of the mass loss versus peak duration curves can be interpreted as a mass loss rate. It increases from 0.5 weight-%/h in a process performed at 0.23 MPa and 170 °C to 2.3 weight-%/h in a process at 0.48 MPa and 160 °C. When applying different peak temperatures (160 and 180 °C) but similar pressures (0.48 and 0.49 MPa) the mass loss rates are almost identical (2.3 and 2.2 weight-%/h). Consequently, the y-intercept and slope again both point towards pressure as the predominant factor in thermal degradation, rather than the temperature. The lower mass loss rate of 1.6 weight-%/h for processes at 170 °C and 0.62 MPa is not fully consistent with this conclusion, but might be caused by saturation effects at mass loss levels that exceed 20 %, because the amorphous carbohydrates are already substantially degraded.

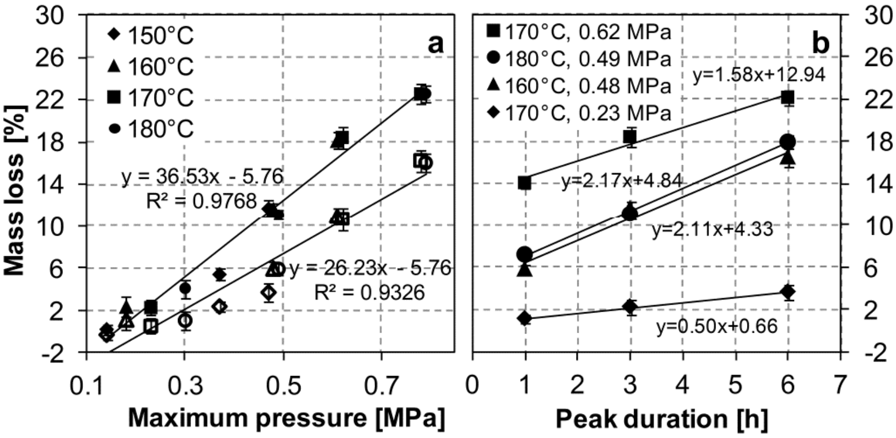

Figure 1: The dependency of mass loss during the process [%] on the process conditions applied. A) Mass loss (open symbols) and corrected mass loss (filled symbols) versus maximum pressure [MPa] for different peak temperatures and constant peak duration of 3 h; B) Corrected mass loss versus peak duration for different temperature and pressure regimes. (± 95 % confidence interval, N=8)

Several studies (Stamm 1956, Burmester 1973, Borrega and Kärenlampi 2008, Rautkari and Hill 2014) have shown that thermal degradation is much faster for processes in closed reactor systems at elevated pressure than for processes in open systems at atmospheric pressure with superheated steam. Various theories exist that might explain these accelerated degradation reactions.

Theoretical, there is the risk that the drying of the wood during the process causes evaporative cooling and hence reduction of the wood temperature towards the dew point temperature of the water vapour (Willems et al. 2015). In that case, the wood temperature would be the decisive factor and water vapour pressure would only indirectly affect wood degradation. However, studies on the thermal modification of beech at atmospheric pressure in superheated steam with peak durations between 2 and 3 h recorded mass losses (based on dry weight without correction for WSC) below 3 % as long as the peak temperature did not exceed 180 °C (Kol and Sefil 2011). In this study, (uncorrected) mass losses above 10 % were even measured after processes at peak temperatures as low as 160 °C, when using elevated pressure. Furthermore, measurements within the treatment vessel (data not shown) clearly showed that the wood temperature closely followed the temperature of the heated walls during the high-temperature holding stage, as long as pre-dried wood (MC 10-15 %) was used.

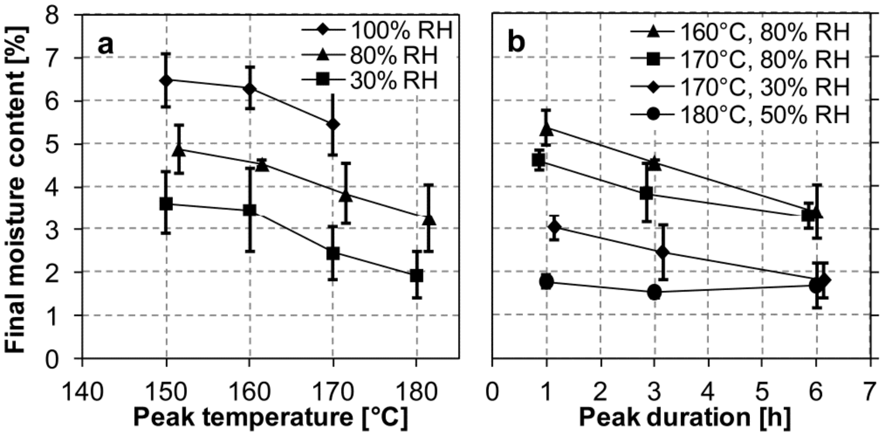

Figure 2: The dependence of final moisture content [%] on the process conditions applied. a) Dependence of the applied peak temperature at different set point RH; b) Dependence of the peak duration for different temperature and RH regimes. Data points were horizontally shifted for better visibility. (± 95 % confidence interval, N=8)

The compressed gas atmosphere in the reactor will presumably not directly affect chemical reactions in the wood, since drying and the formation of volatile organic compounds (VOCs) should lead to a gas flow out of the wood. However, the gas pressure in the closed reactor systems should determine vaporization of water and organic compounds depending on their boiling points, the surrounding temperature as well as the composition and the absolute level of the total pressure. The pressure might thus determine the concentration of water and organic compounds within the wood during the process.

The high-pressure reactor system used in this study was designed to regulate the water vapour pressure (WVP) with the aim of controlling the relative humidity (RH) during the process depending on the temperature. Studies on the sorption behaviour of wood have shown that sufficiently high WVP at elevated temperatures can prevent complete drying of wood and enable equilibrium moisture contents (Lenth and Kamke 2001, Ishikawa *et al*. 2004). Since the wood moisture content could not be measured during the thermal modification process, the final moisture content was recorded instead. It becomes evident from figure 2 A that even at 100 % set point RH, a considerable reduction in moisture content took place. During the process, residual air and volatile degradation products that are formed contribute to the total gas pressure and result in an overestimation of the WVP and the corresponding RH. All process runs have thus been performed at elevated pressure under unsaturated steam conditions. Nevertheless, a clear impact of temperature and set point RH can be observed, with higher final moisture contents for wood treated at high set point RH and low temperatures while lower final moisture contents were evident for wood treated at low set point RH and high temperatures. With increasing peak duration, the final moisture content decreased (see figure 2 B). Although this might indicate that equilibrium moisture contents are not reached, it might also be explained by further modification of the wood over time leading to a change in water sorption.

Accelerated degradation at elevated pressure might thus be linked to the presence of water in the wood during the process. In the presence of water, hydronium ions that are generated by water autoionization act as catalysts for the hydrolysis of lignocellulosic materials at elevated temperatures (Garrote *et al.* 1999). The presence of water in wood also facilitates the thermal softening of the wood. For oven dry wood samples, thermal softening has been found to start at 180 °C with a maximum at 380 °C, while the temperature required decreased with increasing wood moisture content (Chow and Pickles 1971). Borrega and Kärenlampi (2008) hypothesized that thermal softening in the presence of moisture content and the consequent increased mobility of wood polymers lowers the activation energy that is required to induce thermal degradation. Hence, increased WVP enables thermal degradation even at low temperatures. In line with Borrega and Kärenlampi (2008) a negligible mass loss was indeed found at 150 °C and low set point RH, while increasing the set point RH to 80 and 100 % resulted in a corrected mass loss of 6.5 and 13 %, respectively.

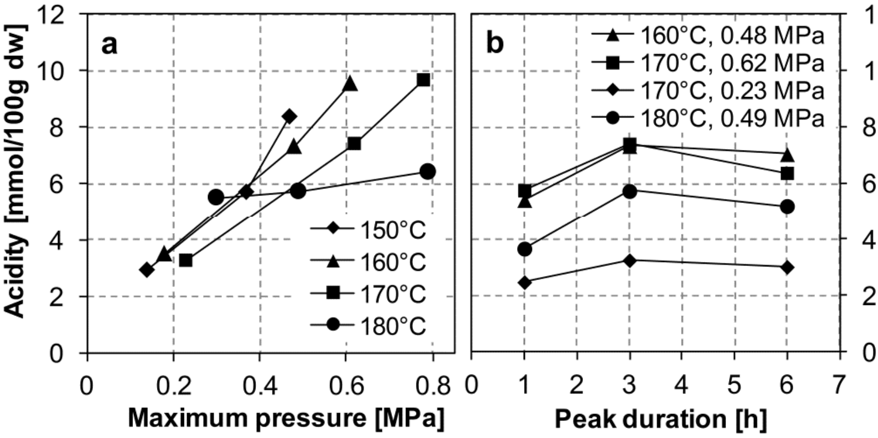

Figure 3: The dependence of acidity [mmol NaOH equiv./100g dw] on the process conditions applied. a) Dependence of the applied maximum pressure for different peak temperatures and a constant peak duration of 3 h; b) Dependence of the peak duration for different temperature and RH regimes.

An alternative theory for the accelerated wood degradation caused by pressure was given by Stamm (1956) and Willems *et al.* (2015), who suggested high concentrations of organic acids as a main cause. Acetic acid is the most prevalent acid in thermally modified wood, with its formation being linked to deacetylation reactions in hemicelluloses at elevated temperatures. This formation is also known to be accelerated in the presence of water caused by hydronium ions created by water autoionization (Garrote *et al.* 2001). Acid catalysed hydrolysis and the dehydration of amorphous carbohydrates are key reactions during the hydrothermal degradation of lignocellulosic materials (Garrote *et al.* 1999; Fengel and Wegener 1984). While organic acids are rapidly vaporized at elevated temperatures at (sub-) atmospheric pressure (Hofmann *et al.* 2013), the surrounding gas pressure and the temperature range might strongly affect their vaporization and thus enable high acid concentrations in the wood during the process. Indeed, figure 3 A shows that the acidity, as a measure of the amount of organic acids being present in the wood, increases with the applied maximum pressure from 1.5 mmol/100g dw. for the unmodified reference up to a maximum of 9.7 after a process at 170 °C and 0.78 MPa. Increasing the peak temperature decreased the impact of pressure. The course of acidity with increasing peak duration, shown in figure 3 B, might indicate finite acid concentrations, as acidity remains almost constant between 3 and 6 h peak duration.

The thermal softening of wood as well as the accumulation of organic acids within the wood are dependent on the presence of water and a sufficiently high pressure. It is thus impossible to separate their individual impact on wood degradation. Both mechanisms might enable wood degradation at low temperatures, as they might compensate for lower temperatures by lowering the required activation energy or by the catalytic effects of organic acids. Processes at low temperatures and high pressure regimes might thus enable sufficient wood degradation to change technologically-relevant wood properties with low energy consumption and without the requirement of a drying step.

CONCLUSIONS

Thermal degradation in closed reactor system, estimated by the wood mass loss during the process, was found to be predominantly determined by pressure, rather than by temperature. It was concluded that pressure determines the vaporization of water and organic compounds from the wood, thus leading to (a) the accumulation of degradation products within the wood, (b) elevated wood moisture contents which facilitate thermal degradation by softening of wood polymers, and (c) high concentrations of organic acids that catalyse carbohydrate degradation.

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Glassy Polymer Formation in Thermally Modified Wood: Effects on Long-Term Moisture and Durability Performance in Service

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Keywords: heat treated wood, glassy polymers, fungal resistance, water sorption, long-term service performance, civil engineering applications

ABSTRACT

It is well-known that the exposure of wood to sufficiently high temperature leads to a reduced equilibrium moisture content (EMC) and improved fungal resistance (durability). This behaviour is generally attributed to chemical changes in lignin and hemicellulose. It is also well-known that these changes are accompanied by a ductile to brittle transition in the wood mechanical properties. This research analyses the effect of glassy state formation in wood polymers, as obtained in thermally modified wood, on the moisture and durability performance. In the thermal modification range aimed at EN350-class I durability performance, moisture and fungal durability are argued to become controlled by the physical state of wood polymers rather than their chemical composition. Glassy polymers may assist the dimensional and fungal stability of thermally modified wood, as characterised by standardized accelerated laboratory tests. However, for long-term dimensional and fungal stability in service, strong crosslinks must prevent the natural (aging) relaxation of the glassy state. The current test methodology for dimensional and fungal stability does not take physical aging effects in wood polymers into account.

INTRODUCTION

Heat treatment of wood in the absence of oxygen is recognized as a viable means of upgrading the moisture and durability performance in service (Hill 2006). In the heating range without dry mass loss (ML=0), there is evidence of the formation of increased hydrogen bonding between wood polymers (Skaar 1988). The limiting EMC at RH=100% has consequently been found to change by 1.1 to 1.3 % EMC for every 10°C increase; this effect can be reversed by water-soaking in vacuum (Obataya *et al*. 2002).

At higher heat treatment intensity, significant ML occurs by the initial release of acetic acid, catalysing further hydrolysis and subsequent dehydration (Fengel and Wegener 1989) and decarboxylation reactions (Bourgeous and Guyonnet 1988). Irrespective of the various heating technologies used (Militz and Altgen 2014), increases in temperature, in partial water vapour pressure or in heating duration appear to lead to a decrease in the equilibrium moisture content (EMC) and an increase in durability in any wood species. These EMC and durability changes correlate directly with changes in the wood elemental composition (Chaouch *et al*. 2013, Willems *et al*. 2013), while ML is more commonly used as a marker of the heat treatment intensity.

EMC decreases with increasing ML, reaching a maximum of typically 50% of the original value before heat treatment. Durability class I according to the European CEN/TS 15083-1 test protocol, indicating full Basidiomycete resistance, appears to be eventually reached for any type of wood species with sufficiently high ML. However, the service performance of thermally modified wood rated as “very durable” does not compare to that of very durable natural timber. Producers often explicitly declare thermally modified wood (TMW) unsuitable for soil or seawater contact, or at least, they do not promote its suitability for these demanding service conditions.

The reason why accelerated fungal tests – including the European soil block test (CEN/TS 15083-2) – are unable to reveal the actual durability limitations of TMW in contact with soil has not yet been fully investigated. TMW is reported (unpublished field experiences) to perform well in contact with soil for many years without noticeable degradation, up to some instant when the wood begins to deteriorate within a relatively short time, leaving it softened, swollen, attacked by organisms and failing on mechanical loading. Wood softening and swelling is considered to be a typical consequence of the fungal decay of wood, however, in an alternative scenario, the glassy wood matrix softens by physical aging and *consequently* fails mechanically or becomes susceptible to fungal attack. Since physical aging is an extremely slow process in glassy solids, this might explain why accelerated fungal decay tests cannot capture this effect. This work critically discusses the possible role of aging in glassy polymers on the durability and moisture performance of thermally modified wood.

WOOD AS A GLASSY POLYMER COMPOSITE

The wood cell wall is composed of densely packed hemicellulose, cellulose and lignin polymers (Fengel and Wegener 1989). In the oven-dry state at room temperature, the mobility of the amorphous part of the cell wall polymers is severely restricted by increased physical bonding. The wood polymer matrix then behaves as a stiff elastic, brittle material (glass). In a humid environment, weak polymer-polymer bonds can be broken in favour of bonds between polymers and water molecules, leading to viscoelastic (ductile) properties (Back and Salmén 1983). The glass-viscoelastic transition occurs near the point of inflection in the moisture adsorption isotherm. Remarkably, this transition point near a relative humidity (RH) of 60% is not shifted by an increase in thermal treatment intensity, despite the higher level of crosslinking in the cell wall (Salmén *et al*. 2008). These crosslinks have, on the other hand, a profound effect on the toughness of wood and cell wall polymer relaxation (González-Peña and Hale 2007, Hill *et al*. 2012, Willems 2014).

EQUILIBRIUM MOISTURE CONTENT OF THERMALLY MODIFIED WOOD

The most important effect of heat treatment on wood is the reduction in hydroxyl (OH-) groups (Tjeerdsma and Militz 2005), causing the limiting EMC near RH=100% to reduce by one water molecule for every lost OH-group (Willems 2014). However, beyond a certain heat treatment level, EMC will not decrease on further OH-group removal (e.g., Chaouch *et al*. 2013) because of a lack of cell wall relaxation, preventing it reaching the *actual* adsorption equilibrium value (Figure 1.). This glassy state is closely related to ordinary hysteresis, where the EMC in desorption is prevented from returning to the adsorption equilibrium value.

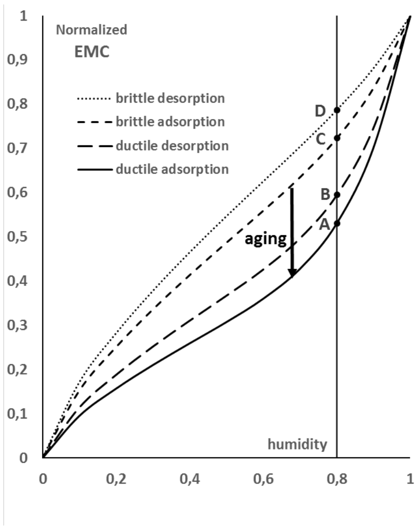

Figure 1: Schematic normalized sorption isotherm shapes. In brittle non-relaxing wood, the adsorption isotherm cannot reach true equilibrium (the adsorption isotherm of ductile wood). The differential swelling of brittle wood is less than that of ductile wood in the high humidity range (compare the derivatives at A vs. C). An aging softening transition may cause full relaxation to the ductile isotherm.

DURABILITY OF WOOD

The durability of natural wood relies on extractable compounds in the cell wall. Each wood species contains a characteristic set of compounds, belonging to various classes of organic substances (Hon and Shiraishi 1991), having various modes of action (Schultz and Nicholas 2000). The durability obtained after heat treatment relies on a different mechanism that appears to be identical for very different wood species, when taking the atomic oxygen-to-carbon (O/C) ratio (Chaouch *et al.* 2013) as a measure of the degree of thermal modification.

In many articles on TMW, durability has been explained by the thermal removal of sugars from wood, observed as ML, and the preferential reduction in the hemicellulose content, consequently reducing the food available for fungi. However, this cannot be maintained in a quantitative perspective. The durability already increases significantly at a ML of 6%, where ample wood sugars remain available to the fungi. Neither are the non-volatilized extractable reaction products of the thermal degradation of wood the cause of durability improvements (Hakkou *et al.* 2006, Karlsson *et al.* 2012).

Microscopic investigations by Tausch (2011) revealed that the mode of fungal decay within each cell wall layer in untreated versus heat-treated wood appeared unchanged in any combination of the wood species, tree zones and basidiomycetes investigated. Apparently, the durability improvement by thermal modification acts via a non-specific mechanism, causing the degradation to proceed more slowly. Willems *et al.* (2013) explained the durability of TMW by an increase in the intrinsic chemical resistance to bio-oxidation, using a semi-empirical thermodynamic correlation with the O/C-ratio (LaRowe and van Cappellen 2011). Moreover, independent oxidation studies using DPPH (Ahajji *et al.* 2009) and TEMPOL (Willems *et al.* 2010) assay methods also indicate an increased chemical oxidation resistance. At mild heat treatment intensity, the oxidation resistance thus seems to be the limiting factor in terms of wood durability. For higher heat treatment intensities, fungal decay eventually becomes completely inhibited, which cannot be quantitatively explained within the oxidation-resistance model.

A reduced EMC, obtained by heat treatment and by other types of wood modification, has been considered to be a possible explanation for durability (Ringman *et al*. 2014). The hygro-expansion, in direct proportion to the EMC, and moisture-induced softening of the elastic cell wall are known to be required for the accessibility of fungal degradation agents in cellulose microfibrils (Flournoy et al 1991). Remarkably, the durability of TMW keeps increasing when EMC has already reached its steady minimum value. In this range, the wood cell wall is in the glassy state.

The significance of the glassy state on the durability of other biological products has been recognized in studies on the shelf-life of carbohydrate-containing food products (Ergun *et al*. 2010) and in the longevity of seeds (Buitink *et al*. 2000). In these cases, the degradation limiting mechanism is a dramatic loss of aqueous diffusivity by glass-formation (Buitink *et al*. 2000). In heat-treated wood, the glass transition temperature of the cell wall is markedly increased by lowered EMCs and the formation of new polymer-crosslinks, which may be the reason behind the complete inhibition of decay (Figure 2.).

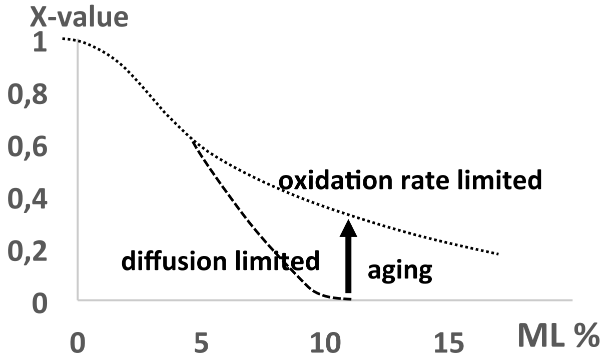

Figure 2: Schematic representation of X-value (as defined in standardized European durability test protocol EN113) versus ML. In brittle non-relaxing wood, decay rates become diffusion limited, whereas they are oxidation rate limited in ductile wood attacked by aggressive wood decay fungi. After an aging softening transition durability performance is adversely changed.

NATURAL VERSUS THERMALLY MODFIED WOOD IN EXTERIOR SERVICE CONDITIONS

Glassy state formation in TMW leads to improved moisture and durability performance ratings by standardized test protocols (Figures 1 and 2). However, it must be appreciated that the glassy state is a non-equilibrium state in non-crystalline solids. In such materials, relaxation is the natural process to gradually lower their free energy. For example, the gradual disappearance (over time and at elevated temperature) of sorption hysteresis is an expression of the relaxation phenomenon (Hill *et al*. 2012, Willems 2014).

In a number of dense hardwoods (e.g., *Afzelia bipindensis*) cell wall relaxation is severely restricted by anatomy and/or the presence of a large volume of extractives in the cell lumens (Willems 2014). Their structure remains stable for many decades, while the extractives provide resistance against decay by micro-organisms. By the lack of relaxation, wood is prevented from reaching the true EMC consistent with its chemical composition – leaving it in a persistent state of "hysteresis". Such wood species present great difficulties in kiln-drying well below the fibre saturation point. However, the combined low differential shrinkage at high RH (Figure 1.), high mechanical strength parameters and high durability make these wood species very suitable in civil engineering applications in temperate climates, without prior air-drying. During periods that cause the wood to dry, tensile surface stresses are induced, which may result in surface checks. These checks which will not propagate deeply beneath the surface, because the moist core volume of the wood is under compressive stress, closing the checks.

In TMW, the natural mechanism of self-limiting surface check propagation can easily become compromised in heating processes during which wood is essentially oven-dried and subsequently remoistened, leaving tensile stresses in the core volume. Although TMW has substantially lower shrinkage ratings compared to natural wood, the combined core tensile stresses and toughness loss by heat treatment will assist check propagation beyond the surface zone. However, heating processes can be designed to avoid reaching oven-drying conditions (Willems 2009), preserving the mechanism of check closure beneath the surface.

Glassy state formation, as a result of increased interactions between the structural wood cell polymers of TMW (Salmén *et al*. 2008), seems essential for durability class I ratings. Unlike the naturally class I durable *A. bipindensis* wood, a softening transition by aging is possible in TMW, which would ultimately reduce the durability performance (Figure 2.). The same aging process will also affect the EMC (Figure 1.), leading to a complex material response, that has yet to be investigated.

The aging process in TMW is deemed to be accelerated by cycling conditions of vapour humidity and uptake of (rain) water. It may be speculated that the softening transition does not occur simultaneously across the wood volume, but local domains of glass-relaxing wood tissue with a tendency to shrink – owing to an EMC reduction – are created within a matrix of intact wood. This would lead to local stresses and micro-cracks that, in turn, increase capillary water uptake, as observed by Scheiding and Direske (2014), providing suitable conditions for further degradation by aging and biological decay.

CONCLUSIONS

Current test results to characterise the moisture and durability performance of thermally modified wood may be only reliable for a limited amount of time after production. It is argued that the durability and dimensional stability performance can benefit from the glassy nature of thermally modified wood, as long as the process of aging does not release the internal stresses within the wood cell wall that are responsible for the stabilisation of the glassy state.

For reliable TMW service life predictions it is recommended that possible aging processes are looked for. If it is expected that relaxation will take place before the estimated service life from current standardized accelerated fungal decay tests, the service life must be re-estimated.

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Surface Chemical Analysis and Water Vapour Sorption of Thermally Modified Wood Exposed to Increased Relative Humidity

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Keywords: Dynamic vapour sorption (DVS), thermally modified wood, X-ray photoelectron spectroscopy (XPS)

ABSTRACT

The surface characteristics of thermally modified wood play an important role in the development of applications involving bonding processes, for example when using thermally modified wood residuals in biocomposites. The objective of this work was to study the surface chemical composition and water vapour sorption properties of thermally modified wood. In particular, an effort was made to study any influence on such properties due to previous exposure to a high relative humidity (RH). The analytical methods applied were X-ray photoelectron spectroscopy (XPS) and dynamic vapour sorption (DVS) analysis. Thermally modified and unmodified spruce samples were prepared. One set of the samples was also initially exposed to a higher RH condition (75% RH, 30 ˚C). The XPS results show differences in the surface chemical composition between the high humidity-exposed and non-exposed samples of both thermally modified and unmodified wood, suggesting changes in the amount of carbons not bound to any oxygen. Interpretations of the results indicate a decrease of extractable or volatile organic components and a relative increase of non-extractable components, for the high humidity-exposed samples. This could be due to the remaining extractives migrating towards, or a redistribution at, the wood surface layer as a result of moisture diffusion. The DVS results show that the thermally modified wood samples that had been exposed to the high relative humidity condition showed a slight decrease in the hysteresis of the sorption isotherms. The opposite trend was seen for the unmodified wood.

INTRODUCTION

Increased insight into the surface characteristics of the processing residuals of thermally modified wood may be useful for the tailoring of new, durable, bio-based composites. A technique used for the chemical analysis of the outermost ca 0-10 nm surface layer is X-ray photoelectron spectroscopy (XPS), also called electron spectroscopy for chemical analysis, (ESCA). XPS analysis has been used to research the chemical composition of the surface of paper and refined lignocelluloses (Dorris and Gray 1978). Moreover, several studies on wood have also been performed. Nzokou and Kamdem (2005) compared the surface of extracted and non-extracted red oak, black cherry and red pine. They concluded that extractives with high carbon content would migrate with the moisture as it moved towards the surface. This would then contribute to changes in the surface chemistry, and thereby have an influence on the wettability and water absorption. It was furthermore stated that the surface energy would also be influenced and less extractives should imply that the surface is more prone to wetting and thus less dimensionally stable. In another study by Inari *et al* (2006), the effect of heat treatment of birch under a nitrogen atmosphere was studied. The results indicated that a decrease could be observed for carbon atoms bound to one single oxygen atom, and an increase was observed for the carbons with bonds to another carbon or hydrogen atom, due to heat treatment. The oxygen to carbon (O/C) ratio decreased due to heat treatment and was explained by degradation of the hemicelluloses and furthermore, from new chemical compounds created as a result of the heat treatment, containing less oxygen. In a study by Johansson *et al*. (1999, 2012), the natural ageing of wood and its influence on the chemical composition of the surface and bulk was researched. The results suggested that no obvious changes in chemical composition could be observed between the surface and the bulk of aged wood, which indicated that the wood matrix inside the wood was well protected from the surrounding environment on the outside of the wood. It was furthermore found that freshly prepared surfaces did not remain stable in terms of chemical composition when exposed to air, X-rays or heat. This could however be moderated by stabilisation of the surface by the use of acetone extraction.

Biocomposites made from a thermally modified wood component bonded or combined with an adhesive or a thermoplastic matrix, can be considered to be more homogeneous than solid wood and also less hygroscopic or sensitive to moisture induced dimensional changes. The interfacial properties of such a wood-polymer combination may however be sensitive to, and will be influenced by, high relative humidity (RH) conditions which will also likely affect the long-term performance of the composite. The water vapour sorption properties of hygroscopic materials can be studied using a dynamic vapour sorption (DVS) technique, where the equilibrium moisture content (EMC) can be detected with high accuracy as a function of RH. Exposure to several sorption cycles has been shown to have influence on the sorption properties of densified and thermally modified wood (Hill *et al*. 2012). From the results of the densified as well as the thermally modified wood, a decrease in the absolute hysteresis (the difference between the adsorption and the desorption isotherms) could be observed for the second and third sorption cycles. The unmodified wood however, did not show this pronounced change in hysteresis between the first and the subsequent sorption cycles.

The objective of this study was to research the chemical composition of the surface of thermally modified spruce as well as its water vapour sorption properties. An effort was also made to study any influence by earlier exposure to a higher relative humidity condition.

EXPERIMENTAL

Materials

The thermally modified spruce (*Picea abies* Karst) studied was prepared according to the ThermoWood® D process. For the DVS analysis, wood components were prepared by grinding the wood in a two-step procedure and then sifting through a 120 mesh (0-0.125 mm) screen. For the XPS analysis, solid wood samples were prepared, due to compatibility and requirements of the apparatus. One set of the ground wood components had been exposed to several dry-humid cycles (75% RH at 30 ˚C, and 0% RH at 30 ˚C) in a previous surface energy study using inverse gas chromatography (IGC), see Källbom *et al.* (2015). In addition to this, one set of both the wood component and the solid wood samples was exposed to a higher relative humidity condition (75% RH at 30 ˚C) before the analyses (Källbom *et al.* 2015).

X-ray photoelectron spectroscopy (XPS)

For the XPS analysis, the solid wood samples were duplicated by dividing in half, where one set were extracted using Soxhlet extraction to remove wood extractives and stabilise the surface prior to the XPS analysis. The other set was left as non-extracted controls. Four freshly cleaved surfaces of the non-extracted samples were prepared; thermally modified (TM), thermally modified exposed (TM exp), unmodified (UM) and unmodified and exposed (UM exp). Additionally, four extracted samples were prepared; thermally modified extracted (TM extr), thermally modified exposed and extracted (TM exp, extr), unmodified extracted (UM extr) and unmodified exposed and extracted (UM exp, extr). Before the XPS analyses, the freshly cleaved surfaces were pre-evacuated overnight with the purpose of stabilising the analysis conditions in ultra high vacuum.

The XPS experiment was carried out using an AXIS Ultra (Kratos Analytical) instrument. A low power setting (at 100W), monochromatic irradiation and neutralization were utilized and an in-situ reference sample of pure cellulose was measured with all sample batches. Survey scans were recorded with 160 eV pass energy with steps of 1 eV, and the high resolution regions were taken with 20 eV pass energy with steps of 0.1 eV. In the data analysis CasaXPS software was used. The elemental surface concentrations were obtained from the low resolution survey data. The carbon chemistry was furthermore evaluated from high resolution C 1s components, fitted with four Gaussian components (C1-4). The four carbons were classified as carbon atoms with 0, 1, 2 or 3 oxygen neighbours, see Table 1, which also shows the distribution of different constituents in wood, related to the four different carbon peaks.

Table 1: Some information of the C1s peak, deconvoluted into four carbon peaks (C1-4) together with the approximate binding energy, functional groups and the percentage distribution of wood constituents related to different carbon peaks

C1s	Approximate binding energy (eV)	Functional groups	Percentage distribution*			
			Cellulose	Lignin	Hemicellulose	Extractives
C1	285.0	C-C, C=C and/or C-H		49		94
C2	286.7	C-O and/or C-O-C	83	49	78	
C3	288	C=O and/or O-C-O	17	2	19	
C4	289.4	O-C=O and/or C(=O)OH			3	6

**Approximate percentage distribution of wood constituents based on theoretical values from Laine et al. (1994) where arabinoglucuronoxylan was used for hemicellulose and oleic acid for extractives*

Dynamic vapour sorption (DVS) analysis

Water vapour sorption isotherms of the wood samples were determined using a dynamic vapour sorption (DVS) apparatus (DVS ET1, Surface Measurement Systems Ltd., London, UK). Two samples of thermally modified wood components were prepared;

thermally modified (TM comp) and thermally modified exposed (TM comp exp). Moreover, two samples of unmodified wood were prepared; unmodified (UM comp) and unmodified exposed (UM comp exp). About 20 mg of wood components were used for each sample analysis. The set temperature was kept constant at 30˚C during the whole analysis. All the sorption measurements started at 0% RH going up to 95% RH in steps of 5% RH. After reaching the level of 95% RH, desorption measurements took place, reversing to 0% RH in steps of 5% RH.

RESULTS AND DISCUSSION

Surface chemical composition

The XPS analysis shows that the exposure to high relative humidity influenced the chemical composition of the surface of both the thermally modified and the unmodified wood samples. In Figure 1, a correlation graph with C1 (C-C/C-H) of total C versus O/C can be seen. All the samples are displayed in relation to theoretical values of the wood constituents. The non-extracted samples, containing more extractives can be found closer to the theoretical point of oleic acid, while the extracted samples naturally, are found closer towards the theoretical point of cellulose. Combining the results from the non-extracted and extracted samples, a theoretical composition of the surface can be proposed. This includes three main groups of compounds representing non-extractable (such as lignin), extractable (such as hydrophilic and hydrophobic wood extractives) and cellulose. As a result of earlier exposure to the high RH condition, the concentration of extractable compounds decreased. At the same time the relative concentration of non-extractable compounds increases. This was seen for both the thermally modified and the unmodified wood. A possible cause for this could be that low molecular weight and hydrophilic wood compounds migrated to, or were redistributed at, the surface layer of the wood samples, induced by water diffusion during drying of these high humidity-exposed samples. This, in turn, implies an explanation for the decreased relative concentration of actual cellulose at the surface, and also the increased concentration of non-extractable components. In another study by Nzokou and Kamdem (2005), it was suggested that the migration, of compounds with high carbon content, to the surface will occur due to moisture movement to the surface from the internal wood structure.

The thermally modified wood seemed to be slightly less affected by exposure to the high relative humidity condition, in terms of changes in the chemical composition of the surface. This can be because changes in chemical composition had already taken place due to the thermal treatment, which induced different prerequisite conditions compared with unmodified wood. Comparing the thermally modified and unmodified samples in Figure 1, it could furthermore be noted that the thermally modified samples, in general, possessed a lower percentage of extractives in relation to the unmodified samples, with the exception of UM extr. However, this is not in agreement with previous studies (Inari *et al*. 2006). The non-exposed extracted samples were all farthest from the theoretical extractive value of oleic acid, which seems reasonable.

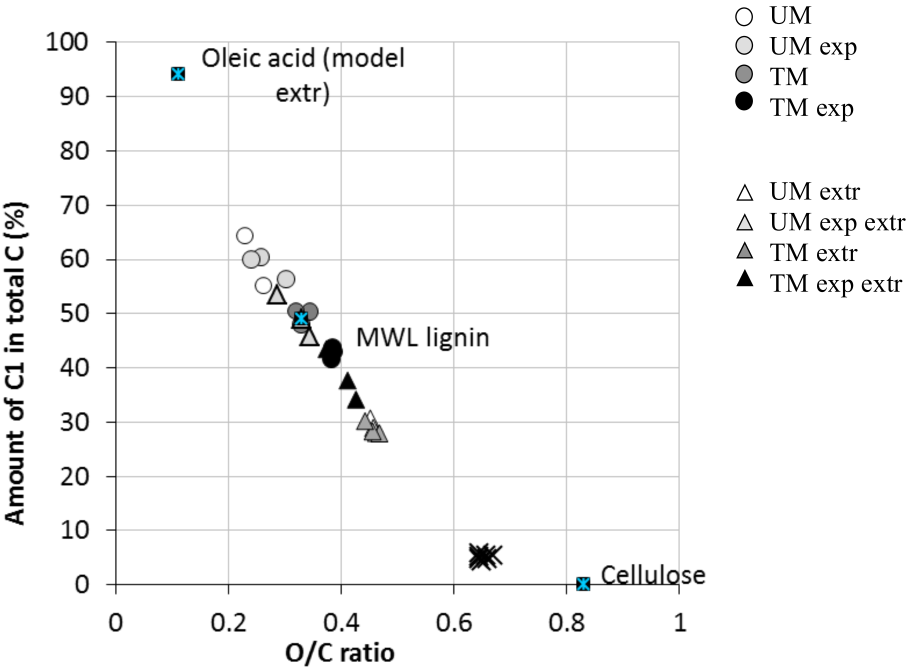

Figure 1: Correlation chart with the amount of C1 in total C (%) versus the O/C ratio of UM, UM exp, TM, TM exp, UM extr, UM exp extr, TM extr and TM exp extr from XPS analyses. The theoretical values for cellulose, lignin, extractives (oleic acid) and data from a cellulose reference (X) are shown

Sorption properties

The DVS analysis shows an apparent decrease in moisture sorption for the thermally modified wood compared with the unmodified wood, which was expected, see Figure 2. There was also a difference in the sorption behaviour between the high humidity-exposed and non-exposed samples both for thermally modified and unmodified wood. The thermally modified wood showed a small increase in the adsorption curve (in the range of 45-95% RH) as a result of earlier exposure to the high relative humidity condition. The unmodified wood on the other hand, showed a small decrease of the adsorption curve at somewhat narrower and higher range of relative humidity due to the earlier high humidity-exposure, see Figure 2. Similar trends were also observed by Hill *et al*. (2012). The desorption curves of the exposed samples were very similar to the desorption curves of the non-exposed samples, both for thermally modified and unmodified wood.

In earlier studies on thermally modified wood, a decrease in sorption hysteresis has been observed as a result of exposure to several water vapour sorption cycles using DVS (Hill *et al*. 2012). This is in agreement with the results obtained in this study for the thermally modified wood, from where, furthermore, it can be concluded that exposure to a higher level of relative humidity of 75% RH (30 ˚C) also had an influence on the water vapour sorption. However, the results for unmodified wood differ in comparison with the results from Hill *et al*. (2012).

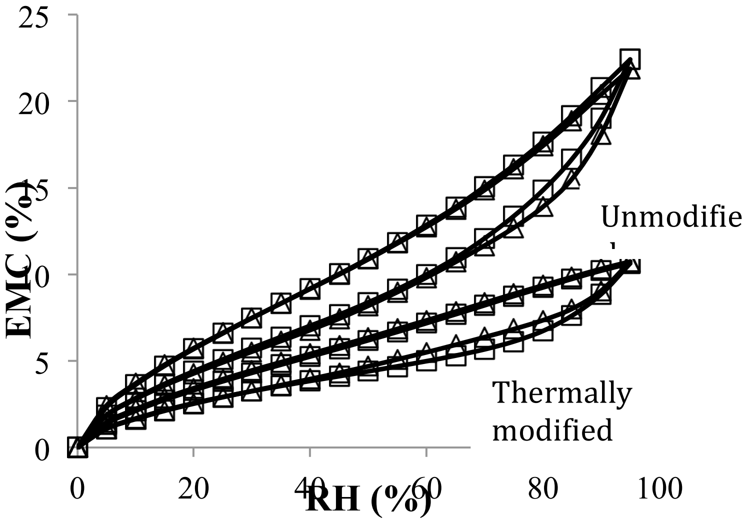

Figure 2: Water vapour sorption isotherms from DVS analyses of thermally modified and unmodified spruce components, both exposed and non-exposed to high relative humidity condition

CONCLUSIONS

The XPS analysis indicates an influence of exposure to a high relative humidity (RH) condition on the surface chemical composition of both thermally modified and unmodified wood. The samples exposed to high humidity showed an increase of non-extractable and a decrease in extractable compounds, and thus also indicate a decrease in cellulose compared with the non-exposed samples. This could be a result of an accumulation of migrated hydrophilic compounds at the surface due to water diffusion in the high humidity-exposed wood samples. Results from the DVS analysis showed changes in sorption isotherm hysteresis for the high humidity-exposed unmodified and thermally modified wood components. This is suggested to be attributable to the chemical composition of the surface, which changed due to exposure to high relative humidity conditions. Changes in the surface chemistry of wood would naturally lead to an alternative structure and thus the amount of accessible hydroxyl groups, furthermore leading to changed wood sorption properties.

ACKNOWLEDGEMENTS

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Hardness, Set-recovery and Micromorphology Studies of Densified and Thermally Modified Wood

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Keywords: densification, hardness, SEM, set-recovery, thermal modification, UV-laser ablation

ABSTRACT

The purpose of the work reported in this paper was to increase the density of Scots pine wood in order to improve its hardness. Density was increased by compressing the porous structure of wood between heated metal plates in the radial direction by 40, 50 or 60% of the thickness. The compressed state was stabilised by thermally modifying (TM) the samples at 200 °C under steam conditions for 2, 4 or 6h. Set-recovery was almost eliminated (<1%) with TM of 6h for samples compressed 40 and 50%. It was discovered that hardness of densified wood was in some cases even three times higher compared to untreated wood. However, the hardness of the densified, non-TM wood was reduced after soaking and drying back to the original untreated level, while TM of 4 and 6h maintained an increased level of hardness.

INTRODUCTION

Wood density is strongly linked to the mechanical properties of wood (e.g. hardness and bending strength), and therefore, it might be beneficial to increase the density of otherwise low-density wood species to improve their properties. In this study, wood density was increased by compressing solid wood samples between heated metal plates to reduce the porosity of wood. Over the past decades several solid wood compression methods have been reported (Seborg and Stamm 1941, Seborg *et al.* 1956, Norimoto *et al.* 1993, Dwianto *et al.* 1998, Inoue *et al.* 1993, Morsing 2000, Kamke 2006) and generally the processes include the same elements; softening of the wood material, compressing (usually in the radial direction) and fixing the sample in the new conformation.

Indeed, without any after-treatment, the compressed state is sensitive to moisture and will recover to some extent when the sample is exposed to high relative humidity (RH) or water-soaking – a phenomenon referred to as set-recovery. A typical after-treatment to fix the compressed state is thermal modification (TM), which reduces set-recovery for two primary reasons: Firstly, in the presence of heat and moisture during TM hemicelluloses, in particular, degrade, which reduces the wood’s hygroscopicity (Dwianto *et al.* 1999, Hill 2006), secondly, TM enables the rearrangement of the molecular bonds (Norimoto *et al.* 1993, Morsing 2000), which enhances the release of the inner stresses created during compression and thereby set-recovery is reduced.

Hardness is known to increase with densification (Inoue *et al*. 1990, Laine *et al*. 2013) however, it is not clear if the improvement in hardness is dependent on the set-recovery. Therefore, the aim of this paper is to examine how compression ratio and TM influence the set-recovery and hardness of densified wood and furthermore, how set-recovery influence hardness.

EXPERIMENTAL

Compression treatment

Scots pine (*Pinus sylvestris*) sapwood samples (RH 65%, 20 °C) were cut from the same board with dimensions of 145mm (longitudinal), 95mm (tangential) and three different (radial) thicknesses (8.5, 10 and 12.5mm). The samples were compressed in the radial direction to 5mm thickness, illustrated in Figure 1.

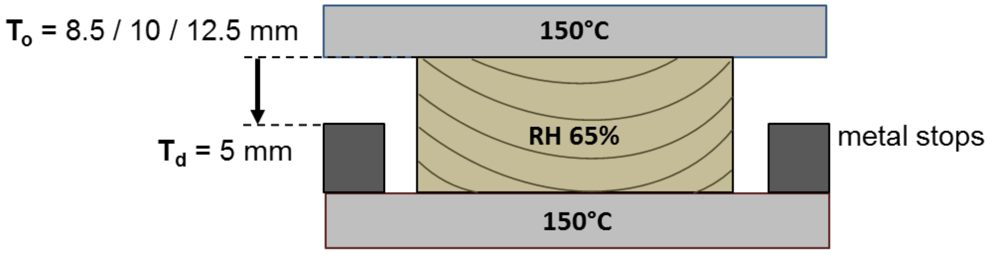

Figure 1: Illustration of the original thicknesses and target thickness controlled by metal stops.

Compression ratios were calculated according to (Eqn. 1), where T_o is the original thickness and T_d the target compressed thickness.

$$\text{Compression ratio [\%]} = (T_o - T_d)/T_o * 100 \qquad (1)$$

Three different original thicknesses resulted in three different target compression ratios 40, 50 and 60%. Densification was performed in an open-press system with fast closure at 150 °C for 1h compression, followed by a 3h cooling period until the press temperature was below 100 °C (to reduce immediate spring back after press opening). Perforated metal plates were used to facilitate the escape of steam generated in the specimens during densification.

Thermal modification

To overcome the issue of set-recovery, the densified samples were thermally modified in steam conditions (atmospheric pressure) at 200 °C for three different times (2, 4 and 6h). Thermal modification was carried out for oven-dried (24h at 103 °C) samples in a treatment chamber from a starting temperature of 120 °C without steam injection, because steam injection below this temperature might cause set-recovery (Rautkari and Hughes 2009). A constant temperature of 120 °C was maintained for 0.5h. Thereafter, the temperature was increased to 200 °C and saturated steam injected into the chamber. The treatment at 200 °C was carried out for 2, 4 or 6h, with continuous steam injection. After thermal modification the samples were once more oven-dried (24h at 103 °C) and mass-loss calculated from the oven-dry weights.

Set-recovery measurement

The purpose of this study was to examine the influence of thermal modification on the set-recovery of densified wood. The set-recovery was measured by comparing the oven-dry (24h, 40 °C) thickness before and after water soaking (24h) and was calculated according to (Eqn. 2).

$$\text{Set-recovery [\%]} = (T_s - T_d)/(T_o - T_d) *100 \qquad (2)$$

In (Eqn. 2) T_s is the recovered thickness after water soaking and oven-drying and T_o is the original thickness before densification and T_d the densified thickness.

Hardness measurement

Hardness was measured in the radial direction according to the Brinell hardness test EN 1534 with minor modifications according to (Rautkari 2012). A steel ball with a diameter (D) of 10mm was applied at a force (F) reaching a nominal value of 1kN after 15s. The force was maintained for 25s and withdrawn completely. According to the standard the diameter of the indentation is measured, however, this stage is rather laborious and difficult to perform accurately on wood, therefore instead, the depth of the maximum indentation (h) was recorded and Brinell hardness (HB) was calculated according to (Eqn. 3).

$$\text{Hardness} = F/\pi Dh \qquad (3)$$

Hardness measurement was performed before and after soaking (24h) to untreated, densified and densified + TM samples which were oven-dry (24h at 40 °C) in order to avoid the influence of moisture content, which is expected to be different for the TM and non-TM samples.

Micromorphology analysis

The micromorphology changes were analysed by SEM before and after set-recovery measurement. The samples were prepared for the microscopy analysis by ultraviolet (UV)-excimer laser ablation technique (Seltman 1995). The UV-laser ablation enables sample preparation without applying mechanical force, which might damage the sample surface, and without inducing moisture in the preparation process, which might cause set-recovery of the samples.

RESULTS AND DISCUSSION

Densification and TM

After densification the average thickness of the wood samples was measured and found to be 5.38mm, indicating an average spring-back of 0.38mm after treatment. Mass losses of approximately 3.2, 4.3 and 5.2% were recorded due to thermal modification for 2, 4 and 6h, respectively. No noticeable set-recovery occurred in the densified specimen following thermal modification.

Set-recovery

The level of set-recovery after water-soaking is expected to be dependent on the level of compression ratio; higher compression ratio resulting in higher level of set-recovery due to higher inner stresses developed during densification (e.g. Blomberg 2006, Kutnar *et al.* 2009). However, in this case the results presented opposite behaviour; for compression ratios (CR) 40, 50 and 60% the corresponding set-recovery values were 60, 58 and 57% (see Table 1). It should be noted, that the differences between the CR groups fall partly within the standard deviation values and therefore the differences can be stated to be statistically insignificant.

Table 1: Set-recovery [%] of samples with different compression ratios and thermal modification times.

Compression ratio	Not thermally modified	Thermal modification time		
		2h	4h	6h
40%	60.4	4.0	2.7	0.5
50%	58.2	5.5	2.0	0.7
60%	56.8	5.7	3.9	1.9

The set-recovery values after thermal modification follow the expected pattern that higher CR indeed results in higher set-recovery. Thermal modification significantly reduced the level of set-recovery to 0.5–5.7%, with longer thermal modification time resulting in lower set-recovery values, which has also been found in previous studies (*e.g.* Inoue *et al.* 1993). It can be concluded, that for samples with densification ratios of 40 and 50% the set-recovery can be almost completely eliminated (<1%) by 6h thermal modification.

Micromorphology

In order to find evidence of possible cracking in the cell-wall SEM analysis was performed for densified and thermally modified samples before and after soaking and drying of the samples. Figure 2 presents example SEM images of a densified and thermally modified sample before and after soaking from the same position in the cross-section of the sample.

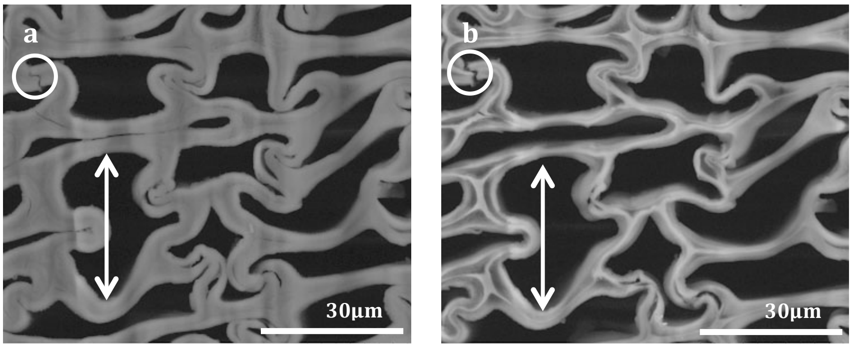

Figure 2: SEM image of through thickness densified Scots pine sapwood with compression ratio 40% and 2h thermal modification (a) oven-dry before soaking, (b) oven-dry after soaking.

Figure 2 shows that very little changes in the cell dimensions and shape occurred after soaking and drying of the sample (see same sized arrow in both images). Evidence of possible cell-wall cracking was found for example in Figure 2a in the circulated area where a micro-crack seems to open-up after soaking and drying in 2b. Another interesting phenomenon is that repeated SEM imaging from the same position seemed to have damaged the sample surface in Figure 2b, where the cell-walls appear thinner than before soaking in Figure 2a. This phenomenon was observed only in the position where the SEM image was taken repeated times especially in the case of thermally modified samples. Such behaviour might be caused by degradation products still remaining in the cell-wall after the modification process which after the soaking have disengaged from the sample surface, either during the soaking and drying procedure or in the SEM. This was further studied by analysing the oven-dry weight loss before and after soaking. Indeed there was a minor loss in oven-dry weight after soaking; however, thermal modification did not seem to influence the weight loss due to soaking. In fact, the highest weight loss was found with the densified and non-TM samples (1.3%), while TM seemed to slightly reduce weight loss; the average weight losses for the samples thermally modified for 2, 4 and 6h were 0.93, 0.90 and 0.77%, respectively. These weight loss values suggest that indeed some loss of material occurs during soaking and drying. However, based on the SEM imaging it was expected that longer TM time would increase weight loss, since that is where the most dramatic changes were seen. Based on these results it is unclear what caused the loss of material in SEM, while the most probable cause was the combined action of SEM imaging and soaking and drying of the samples.

Hardness

In previous studies (Rautkari 2012, Laine *et al.* 2013), densification has been found to increase hardness of wood which was also the case in this study. The average Brinell hardness values are presented in Figure 3 for the untreated, densified and TM samples. The average hardness for untreated samples was 23.2 N/mm^2, while the hardness for densification ratios 40, 50 and 60% were 36.1, 66.7 and 66.2N/mm^2, respectively (including both non-TM and TM samples). This result suggests that hardness can be significantly increased by compressing 40% and even tripled by compressing 50% of the thickness; however, further increase of the compression ratio to 60% does not significantly improve hardness.

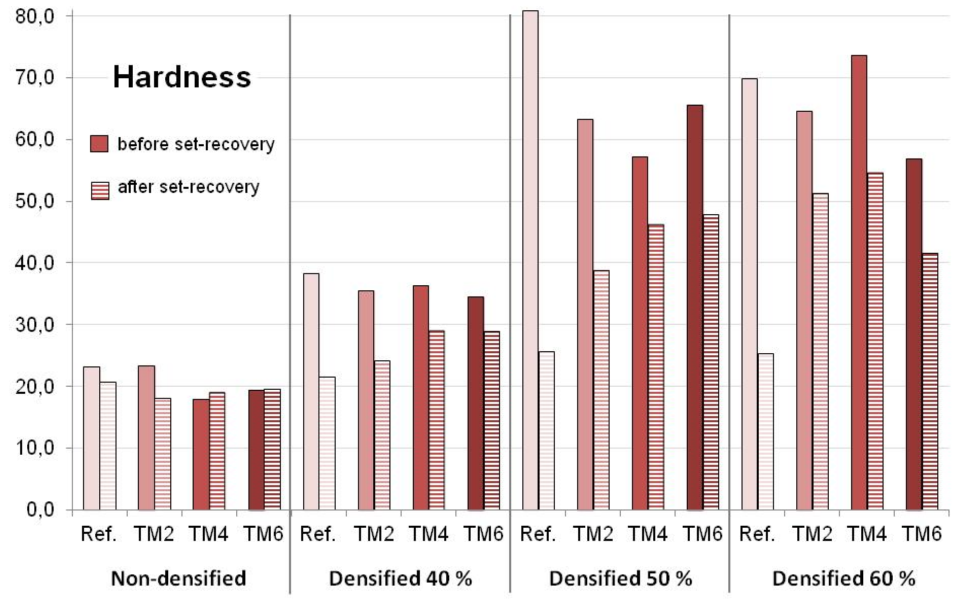

Figure 3: Average Brinell hardness of samples that were non-densified or densified 40, 50 or 60% of their thickness, and non-TM (Ref.) or TM for 2, 4 or 6h.

Average hardness values for (non-densified) thermally modified samples for 2, 4 and 6h were 23.3, 17.8 and 19.4, suggesting that 2h treatment does not significantly influence the hardness, while longer treatment time reduces it slightly. Soaking of the samples generally reduced hardness and the most dramatic decrease was seen for the densified (non-TM) samples, with over half of the hardness reduced after soaking almost back to the original untreated state. TM seems to reduce the influence of soaking on the hardness; in general, there is a slight reduction in hardness after soaking for non-TM and 2h-treatment, while with 4- and 6-hour-treatments the hardness reduces clearly less (or even increases in the case of non-densifed wood). These results produce more evidence that increase in hardness due to densification is clearly dependent on the reduced porosity in densified wood. As the deformation is recovered and porosity increases, hardness is reduced, while with TM the cell-walls are locked in the new compressed position with minimal set-recovery and therefore hardness is not reduced even after soaking of the samples.

CONCLUSIONS

In this study Scots pine solid wood was densified 40, 50 and 60% of the thickness and thermally modified 2, 4 and 6h at 200 °C in steam conditions. TM significantly reduced set-recovery of the densified samples and set-recovery was almost eliminated (<1%) with 6h treatment (for CR 40 and 50%). Minor cracking of the cell-walls were discovered in the SEM analysis of the densified sample cross-section, however, with TM the shape of the deformed cells maintained even after soaking and drying of the samples. Brinell hardness of the samples even tripled due to densification, however, without post-TM set-recovery of the samples reduced the hardness almost back to the original value before densification. Using TM after densification the hardness value maintained at a higher level even after soaking and drying, especially with the longest treatment time 6h.

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Thermal Modification of Poplar Veneers in Vacuum Conditions

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Keywords: FT-NIR, poplar, thermal modification, vacuum, veneers

ABSTRACT

Poplar wood has the potential to be used for many purposes since it is one of the most economical species, is easy to process, has low density and has a uniform light colour. However one of the main problems noticed during industrial manufacturing and further use of the products derived from the material is its high hygroscopicity. Vacuum thermal treatment is proposed here to improve dimensional stability, decrease hygroscopicity and change the colour of poplar veneers used for plywood manufacture. In total, the processing of 38 batches, with various treatment conditions was carried out. Samples were characterized in terms of their appearance (colour), physical (mass loss and equilibrium moisture content) and chemical properties (near infrared spectra). All the measured veneer characteristics differed with thermal modification, even if the trends and kinetics of the changes varied between parameters. Selected chemometric techniques: Principal Component Analysis (PCA) and Partial Least Squares (PLS) were used for data evaluation. PCA allowed direct comparison of the effect of process parameters on the chemical composition of poplar veneers. PLS proved the potential of near infrared spectroscopy in the development of robust prediction models for mass loss and equilibrium moisture content. Such methodology might be helpful in the development of on-line process control and for further optimization of the thermal treatment of poplar veneers at industrial scale.

INTRODUCTION

Poplar is a fast growing species, widespread in plantations with a rotation period of 5 to 20 years. It is economically important for several industrial and ecological reasons. In Europe poplar plantations cover about 940,000 hectares and approximately 90% of their production is used for the manufacture of plywood, sawn timber, pulpwood, fuelwood and biomass for energy (Nervo *et al.* 2011). One of the main problems noticed during industrial manufacturing and further use of the products derived from poplar is the high hygroscopicity of the wood material. Poplar plywood tends to deform with the adsorption of moisture (Murata *et al.* 2013).

Thermally modified wood (TMW) is an example of wooden products that follow the trend of substituting traditional resources with those with novel or improved characteristics. According to CEN/TS 15679:2008 TMW is defined as a timber in which the chemical composition of the constitutive woody polymers and wood physical properties are modified by exposure to high temperatures (usually from 160 to 230°C) under conditions of reduced oxygen availability. Wood modified in this way possesses superior durability against decay and weathering, enhanced dimensional stability, constant colour, reduced thermal conductivity and lowered equilibrium moisture content.

Several researchers have reported the advantages of thermally treating veneers to improve dimensional stability, decrease hygroscopicity and change their colour (Bak and Németh 2012, Zdravković *et al*. 2013, Lovrić *et al*. 2014, Goli *et al*. 2015). However wooden surfaces exposed to high temperature can experience surface inactivation and consequently lead to adhesion problems during plywood manufacturing (Ayrilmis and Winandy 2009). The thermo-vacuum process is an alternative technology for the thermal modification of wood where the reduction in oxygen concentration inside the reactor necessary to avoid wood combustion is obtained by applying a vacuum. The absence of volatiles and water vapour, being the result of their continuous removal by vacuum pump, ensures a lower rate of wood mass loss (ML), assures high energy efficiency, less corrosion and a lower reduction in mechanical properties compared to alternative treatment technologies (Allegretti *et al*. 2012).

Fourier Transform Near Infrared Spectroscopy (FT-NIR) is a technique capable of the fast, non-destructive measurement of organic materials. Quality assessment of thermally treated wood by means of NIR has previously been investigated by several researchers (Schwanninger *et al*. 2004, Esteves and Pereira 2008, Bächle *et al*. 2012, Sandak *et al*. 2012). Spectroscopy often serves in the development of Partial Least Squares (PLS) models based on NIR spectra for indicators of the degree or extent of thermal modification: mass loss (ML) and equilibrium moisture content (EMC). Promising results obtained previously by Esteves and Pereira (2008) and Sandak *et al*. (2015) suggest the possibility of using spectroscopy for the quality control of thermally treated wood.

The research presented here is an attempt to record the detailed characterization and evaluation of poplar veneers modified under vacuum conditions. The goal of this work was to evaluate the influence of temperature, time and pressure on the principal indicators of the thermal modification process such as ML and EMC of the material investigated. Within the scope was the development of PLS models that might be used for the quality control of treated veneers in industrial scale production.

EXPERIMENTAL

Samples preparation

Rotary-cut veneer sheets of the poplar clone 'I-214' (*Populus ×canadensis* Moench) were used for the preparation of experimental samples. One sheet of plywood was prepared for each treatment. The veneers were cut to dimensions of 360 mm x 150 mm x 2.5 mm and were characterized both before and after vacuum thermal treatment.

Thermal treatment

Thermal treatment was performed in a prototype plant described previously by Sandak *et al*. (2015). Electrically heated aluminium plates, which produce heating of the conducting type, were used. The heating and cooling ramps were kept constant at 60°C/h. The ventilation was disabled so that the test chamber only acts as a sealing system for the vacuum. Each modification process consists of three phases; 1) wood drying, 2) thermal treatment and 3) wood conditioning. In one case (batch #31) the process was stopped after reaching the maximum temperature and the thermal treatment phase was omitted. The treatment time value, presented in Table 1, is equal to 0 in this case. The experimental set-up and an example of samples are presented in Figure 1.

Figure 1: Veneer treatment set-up (a) and experimental samples after thermal treatment (b)

In total the processing of 38 batches, with various treatment conditions (temperature ranging from 150°C to 240°C, pressure: 100, 250 or 1000 mbar and duration from 0.5 to 22.5 hours), was performed (Table 1).

Table 1: Combinations of the performed tests

batch number	**#1**	**#2**	**#3**	**#4**	**#5**	**#6**	**#7**	**#8**	**#9**	**#10**	**#11**	**#12**	**#13**
T max [°C]	240	238	238	238	195	150	174	192	174	213	240	253	239
time [hours]	1.5	1.5	1.5	1.5	6.1	12.4	6.4	22.2	22.5	22.2	22.3	1.1	1
pressure [mbar]	1000	250	100	1000	1000	250	1000	250	250	250	250	250	1000
batch number	**#14**	**#15**	**#16**	**#17**	**#18**	**#19**	**#20**	**#21**	**#22**	**#23**	**#24**	**#25**	**#26**
T max [°C]	239	239	238	241	239	239	212	203	194	182	174	165	155
time [hours]	0.5	2.12	0.24	2.22	1.07	0.5	1.08	1.1	1.07	1.07	1.07	1.07	1.07
pressure [mbar]	1000	1000	1000	250	250	250	250	250	250	250	250	250	250
batch number	**#27**	**#28**	**#29**	**#30**	**#31**	**#32**	**#33**	**#34**	**#35**	**#36**	**#37**	**#38**	
T max [°C]	149	223	213	213	211	213	194	173	214	175	240	217	
time [hours]	1.07	1.07	2.24	4.3	0	6.42	6.1	6.4	4.7	12.9	6.6	4.8	
pressure [mbar]	250	250	250	250	250	250	250	250	100	250	250	1000	

Sample characterization

The resulting material was analyzed before and after each treatment in order to determine the modification rate on the physical/chemical wood properties induced by the process.

<u>Physical properties</u>

Mass loss (ML) was determined by weighting each sample before the treatment and immediately after it, ensuring that the wood was absolutely dry (0% moisture content).

The Equilibrium Moisture Content (EMC) of the treated and untreated samples was calculated according to the ISO 3130 standard.

Colour measurement

A MicroFlash 200D spectrophotometer (DataColor Int), suitable for the direct determination of the CIE L*a*b* colour coordinates was used for measurement over an 18 mm diameter spot with a standard light source, D65, and an observation angle of 10°. Each sample was measured in 10 zones. The standard deviation of such measurement was considered to be an indicator of the instrument reliability and the texture variability of the material.

NIR measurement

A VECTOR 22-N Fourier transform near infrared spectrometer (Bruker Optics GmbH, Ettlingen, Germany) equipped with a fibre-optic probe was used for the collection of spectra. The spectral range measured was between 4000cm^{-1} and 12000cm^{-1}. The spectral resolution of the spectrometer was set to 8cm^{-1}. The spectral wave number interval was 3.85 cm^{-1} with zero-filling = 2. Each spectrum was computed as an average of 32 successive scans in order to minimize the measurement error. The FT-NIR measurements were performed in air-conditioned laboratory (20°C, 65%RH), five times on each sample. OPUS 7.0 (Bruker Optics GmBH) software was used for the collection of spectra, pre-processing and data mining. A QUANT2 module was used for chemometric data evaluation.

RESULTS AND DISCUSSION

As expected, heat treatment affected the wood colour; the wood becomes darker uniformly all over the piece. Figure 2 present the changes in the lightness of the samples treated under similar conditions (≈ 210ºC and 250mbar) for various periods (up to 22 hours). It is clearly visible that the drop in L* is correlated with the duration of thermal treatment. Only samples from batches #29 and #30, which were treated for 2.2 and 4.3 hours have a similar ΔL. An analogous trend was also present for other treatment configurations. The changes in colour are due to a combination of the degradation of chemical constituents (mainly hemicelluloses) and the migration or removal of extractives, low molecular weight sugars and amino acids (Akgül and Korkut 2012).

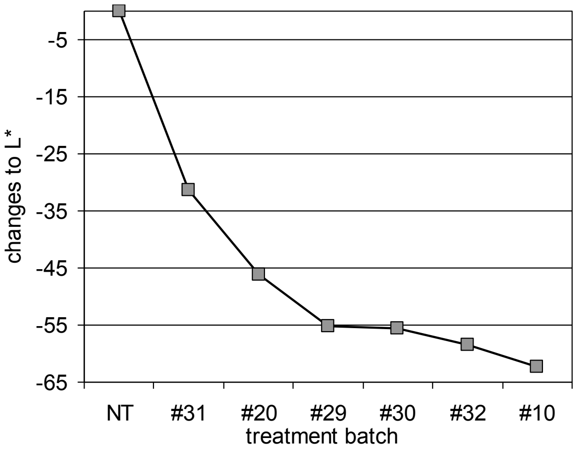

Figure 2: Changes of L of veneers treated in ≈ 210ºC and 250mbar for different durations*

Treated wood has significantly lower EMC compare to untreated wood. The decrease in the moisture uptake is due to the decrease in its water storage capacity (Bak and Németh 2012). It is an effect of the reduction in the accessibility of the hydroxyl groups of the wood carbohydrates, degradation of the hemicelluloses and their conversion into less hygroscopic furan-based polymers and polycondensation and crosslinking of lignin (Sandberg *et al*. 2013). The EMC decrease depends on the treatment temperature, time and pressure. Thermal treatment also influences mass loss, which according to Ferrari *et al*. (2013) may be a reliable indicator of the wood modification progression. ML is closely correlated with a decrease in EMC and leads to a reduction in wood density. It is a result of polymer degradation and evaporation during the heat treatment process. The mass losses in samples investigated varied from 0% (in case of veneers treated at 150°C for 1 hour, 250 mbar) to 48% in the case of long treatment (22h) at high temperature (240°C) and 250 mbar. The same treatment parameters (240°C, 250 mbar), but shorter time (6.6h) resulted a 24% mass loss. A similar effect (22% ML) was obtained at a slightly lower temperature (213°C), however with a longer treatment time (22h).
Figure 3 presents an example of Principal Component Analysis performed on NIR spectra of veneers treated with various process parameters. It is clearly visible that all groups are clearly separated; however, untreated samples are clustered close to samples treated at relatively low temperature (batch #26). This group also includes samples after low temperature treatment, though conducted for a long period (batch #9, 22h). Veneers treated at temperatures above 200ºC are clustered together with the exception of veneers treated at 240ºC for 6.6 hours (batch #37). PCA in this case allowed direct comparison of the effect of process parameters on the chemical composition of poplar veneers.

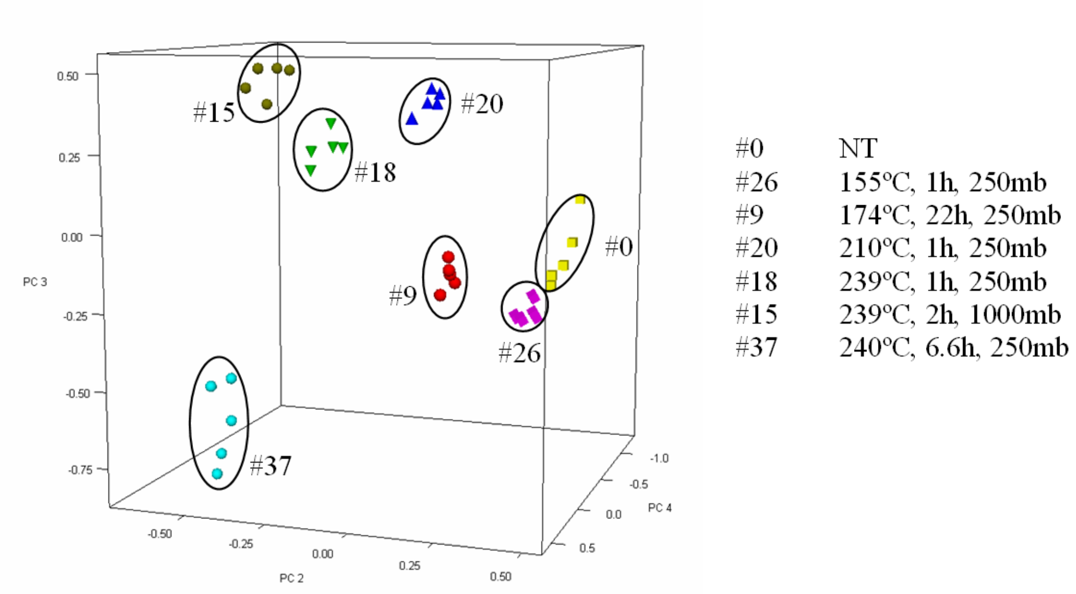

Figure 3: Example of PCA analysis performed on NIR spectra

Partial Least Squares (PLS) can be used to create models with good predictive power, avoiding noise and maximising information (Danvind 2002), and are therefore often used for computing regression models linking near infrared spectra and reference values corresponding to diverse wood properties. Predictive models for ML and EMC were developed within this research. Mass loss and equilibrium moisture content values were implemented into the QUANT2 software module as the reference variables. Each model was characterized by the coefficient of determination (R^2), root mean square error of cross-validation (*RMSECV*), residual prediction deviation (*RPD*), bias (the average difference between the instrumentally measured values and the reference values) and rank (number of principal components used). The high values of the determination coefficients ($R^2 > 0.96$ for both parameters) and $RPD = 5.15$ for ML and $RPD = 5.26$ for EMC respectively, confirm the superior performance of the PLS (Alves *et al.* 2012). Figure 4 presents the regression of the predicted versus measured ML values.

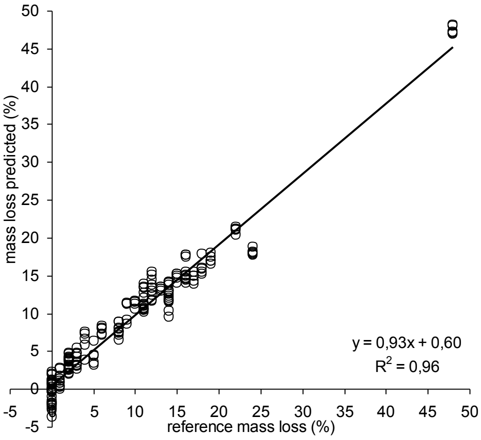

Figure 4: PLS predicted versus measured values of ML of thermally modified veneers.

CONCLUSIONS

Accurate characterization of the final product quality after wood thermal treatment is still of great concern to both producers and consumers. All the veneer characteristics measured differ with the thermal modification process, even if the trends and the kinetics of the changes varied among the parameters. Multivariate data analysis and chemometric modelling allowed for an understanding of the process mechanism and its kinetics and might be used for the selection of optimal process parameters. NIR, as a fast and non-destructive technique, was effectively used to predict selected wood physical properties, considered as reliable indicators of the wood modification progression. The prediction errors of the validation models based on FT-NIR spectra were relatively small (1.8% and 0.29% in case of ML and EMC respectively). The corresponding coefficients of determination were $R^2 > 0.96$ in both cases. Preliminary results support the assumption that PLS models of NIR spectra are suitable for the quality control of vacuum thermally treated veneers and might be used at an industrial scale in the case of further implementation towards on-line process control.

ACKNOWLEDGEMENTS

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Evaluation of Differences in Thermal Modification as a Result of Depth Profiling. Preliminary Investigations into Material Treated Using the Firmolin ™ Process

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Keywords: analysis, dynamic vapour sorption (DVS), scanning electron microscopy (SEM), thermal modification

ABSTRACT

FirmoLin™ is one of the commercialised thermal modification processes in Europe (Willems 2009). On exposure to high temperatures, without oxygen, wood is slowly decomposed and modified at a controlled rate. Consequently, parts of the wood cell walls that digestible by fungi are partly removed and partly converted into very stable compounds. The modified wood is more water repellent and has an increased antioxidant capacity, all adding to the resistance to wood decay. Browning reactions similar to those during the baking of foods will occur, which is responsible for the yellow-brown colouration of treated timber. All modifications take place at the molecular level of the cell wall so that the cellular structure of wood should remain unaltered. General trends with increasing steam treatment temperature and pressure are an increased resistance to fungi, increased dimensional stability and an increased dark colour. Through micromorphological studies, dynamic vapour sorption studies, the use of Fourier Transform Infra-Red (FT-IR) Spectroscopy and analysis of volatile components, this paper aims to provide an overview into the chemical changes occurring within Firmolin™ samples. The results showed that the Firmolin™ process results in a uniform treatment throughout the samples assessed, with evidence of limited microstructural change resulting from the treatment.

INTRODUCTION

The use of thermal modification as a means of modifying wood has become well established since its earliest scientific considerations (Tiemann 1915, Kollman 1936). There have been several instances of reviews into the thermal modification of wood (*e.g*. Rapp 2001, Hill 2006, Esteves and Pereira 2009), to which the reader is guided for further reading. Thermal modification of wood takes place at the ultrastructural level of the cell wall. The main constituents, cellulose, hemicellulose and lignin, are modified by three main chemical reactions – namely hydrolysis, dehydration and cross-linking (Fengel and Wegener 2003), usually occurring in this order as the modification proceeds. On dry heating, dehydration and cross-linking processes dominate, since the moisture necessary for hydrolysis is lost through evaporation in high temperature processing. This problem was solved in the PLATO process (Tjeerdsma *et al.* 1998) by employing separate treatment stages for hydrolysis in saturated steam (165 ºC) and for curing in dry heat (185 ºC), with an intermediate low-temperature conventional drying step. Burmester (1973) showed in his FWD (Feuchte-Wärme-druck) process that thermal modification was possible in a pressure autoclave with high pressure superheated steam treatments on kiln dried wood (MC=12-14%). In an early stage of this process acetic acid is liberated from the wood cell wall and remains trapped inside the timber under the action of the external steam pressure. Acetic acid acts as a catalyst in all three reaction types, which enables fast modification at moderate temperature.

To avoid the evaporative loss of the acetic acid catalyst, the FWD process requires a minimal gas pressure, whilst avoiding core stress problems within the wood requires the maintenance of a sufficiently high moisture content. Both of these conditions are met in the Firmolin™ process with pure steam in hygroscopic equilibrium with the moisture in wood. The pressurised superheated steam has three functions: 1: heat transfer medium – heat transfer rates are in direct proportion to pressure, 2: prevents the vaporisation of organic acids (acetic and formic) in wood, serving as catalysts for the thermochemical reactions at low temperature (relative to those used in atmospheric heating) and 3: control of moisture content, avoiding oven-drying conditions that would otherwise lead to severe shrinkage-stresses. The process is shown schematically in Figure 1.

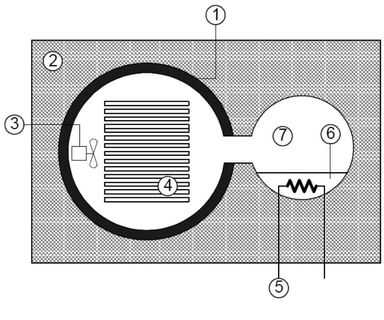

Figure 1: Schematic illustration of the Firmolin™ Process. The controllability of the process is achieved by regulating the temperatures of the vessel wall and the water reservoir. 1 = Heating jacket of the autoclave, 2 = Thermal insulation, 3 = Fan, 4 = Timber stack, 5 = Heating element, 6 = Water reservoir, 7 = Water vapour

EXPERIMENTAL

Blocks of Norway spruce (*Picea abies*) and beech (*Fagus sylvatica*) and boards of radiata pine (*Pinus radiata*), Norway spruce (*Picea abies*) and Obeche (*Triplochiton scleroxylon*) sourced from various locations were all treated using the Firmolin™ process by heating and maintaining conditions during a holding phase (between heating and cooling). The conditions used were T=173 °C at a steam pressure of 6.7 bar for a duration of 4 hrs. All residual air was displaced with pure steam. This treatment was used for all samples. The total process run was completed in 23 hours.

DVS analysis

Small wood samples of approximately 5 mg were cut using a razor blade from untreated and thermally modified boards for the water vapour sorption analyses. The spruce samples consisted of both earlywood and latewood, but for radiata pine only earlywood. Analysis of the spruce and radiata pine was carried out using DVS Intrinsic and DVS elevated temperature (ET) instruments (Surface Measurement Systems, London, UK) respectively. First the samples were placed in the sample pan and then dried under a dry nitrogen gas flow (DVS intrinsic: 100 sccm, DVS ET: 200 sccm) until the moisture content (MC) was 0% (at 25 °C), followed by a sorption cycle with 5% RH steps to a maximum of 95% RH and desorption cycle with a reverse sequence. Both DVS instruments maintained a constant RH until the change in the sample mass was lower than 0.002% per minute over a 10 min period to ensure constant equilibrium condition after each RH steps.

Volatile analysis

In order to determine the presence of volatile components, a sorption extraction was performed using a 5cm^3 50/30µm DVB/CAR/PDMS Stableflex SPME fibre. Samples were contained in a 20 cm^3 headspace vial, and left to equilibrate at 40 °C for 10mins, after which SPME fibre was introduced and left to adsorb volatiles for 40mins. After adsorption, the fibre was desorbed manually for 1 minute in the injector. For analysis, a gas chromatograph (Clarus 680) coupled to a mass spectrometer (Clarus 600 C) was used with a split ratio of 2:1 and a GC injector temperature of 250 °C. An Agilent VF5-MS5 column was installed in the GC-MS. The GC-MS system was controlled by Turbomass software equipped with NIST/EPA/NIH mass spectral library. The following temperature program was used for the gas chromatographic run: Original oven temperature 40 °C held for an initial 2.5mins, followed by a temperature increase of 5 °C/min up to 200 °C, then increased by 10 °C/min to 240 °C, and held for 5min at the final temperature (total chromatographic run time of 43.5 minutes). The mass spectra were recorded in EI mode, scanning m/z 40-600 in 1 second. Between extractions, the fibre was conditioned following the manufacturer's instructions, exposing the fibre to 270 °C for 30 minutes in a GC injector under a constant flow of nitrogen.

FT-IR analysis

An Attenuated Total Reflection-Fourier Transform Infrared (ATR-FTIR) Spectrometer was used to analyse the untreated and thermally modified samples. All measurements were performed in air at room temperature using two measuring points for each sample. The equipment used was a Perkin-Elmer Spectrum 2000 FTIR equipped with a MKII Golden Gate, Single Reflection ATR System (Specac Ltd, London, UK). The ATR crystal was a MKII heated Diamond 45° ATR Top Plate.

SEM analysis

Prior to SEM analysis, samples were prepared using an UV (or excimer) laser technique to prevent any microstructural damage occurring from the mechanical preparation of material, as explained in previous studies (Wålinder *et al.*, 2009). Thus, a pulsing krypton fluoride (KrF) exciplex laser (Lumonix PM886) was used at a wavelength of 248 nm, with the resulting laser beam passing through a series of lenses and masks to create a focal point on the surface of the material being excimed. The laser pulse width was 20 ns, with pulse frequencies varying between 5 and 10 Hz. The result of this was output pulses with energy levels of approximately 300-400 mJ. The microstructures of the excimed materials were analysed using a scanning electron microscope (Hitachi Tabletop Microscope TM-1000).

RESULTS AND DISCUSSION

DVS analysis

Figure 2 shows the typical sigmoidal shaped sorption isotherms of the untreated and thermally modified spruce (Figure 2a) and radiata pine (Figure 2b). The sorption isotherm of the untreated spruce was almost identical to that of the radiata pine. Only the hysteresis (Figure 3) was approximately 1% higher in the untreated radiata pine. Unsurprisingly, thermal modification reduces the equilibrium moisture content (EMC) of the material. At RH 95%, the EMC of the spruce dropped from 21.9% in unmodified form to 8.8% after treatment and for radiata pine from 21.7% to 10.8%. Thus, there appears to be a greater effect of the Firmolin™ treatment on the spruce samples analyzed.

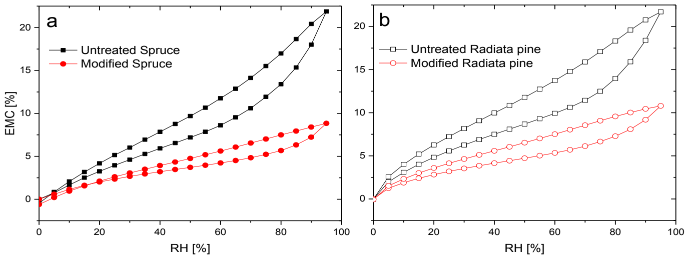

Figure 2: Sorption isotherms for (a) untreated and thermally modified spruce; and (b) untreated and thermally modified radiata pine

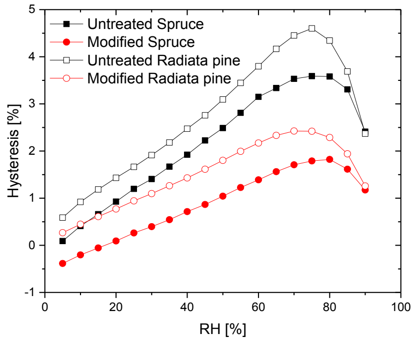

Figure 3: Hysteresis for untreated and thermally modified spruce and radiata pine

In earlier studies (Hill *et al*. 2012, 2013) several sorption cycles were performed and it was found that there are differences between first and subsequent cycles for thermally modified wood, but not for untreated wood. It was discussed that the change in the isotherms could be attributed to a stress relaxation process at high cell wall moisture contents. The change occurred on the adsorption cycle and involves an increase in the EMC from the first to second sorption cycle. The same behavior was not measured in this study, but this phenomenon should be seen in these samples also, if subsequent cycles were to have been performed. Therefore, the difference in hysteresis between modified and untreated samples (Figure 3) can be explained by an increase in the storage of stress in the modified samples, as in earlier studies the hysteresis decreased after sequent humidity cycles. In Figures 2a and 3 with thermally modified spruce the EMC is lower than 0% and the hysteresis at low RHs is also negative during desorption. This is caused by trapped water that could not dry in the first place at beginning of the experiment.

Volatile analysis

The chromatograms obtained for the samples are shown in Figure 4, corresponding to untreated radiata pine (1), modified radiata pine (2), untreated spruce (3), modified spruce (4), untreated beech (5), modified beech (6), untreated obeche (7) and modified obeche (8). Analysis of results indicated that the thermal treatment removed the majority of terpene-based volatiles present within the wood species, as indicated in Table 1.

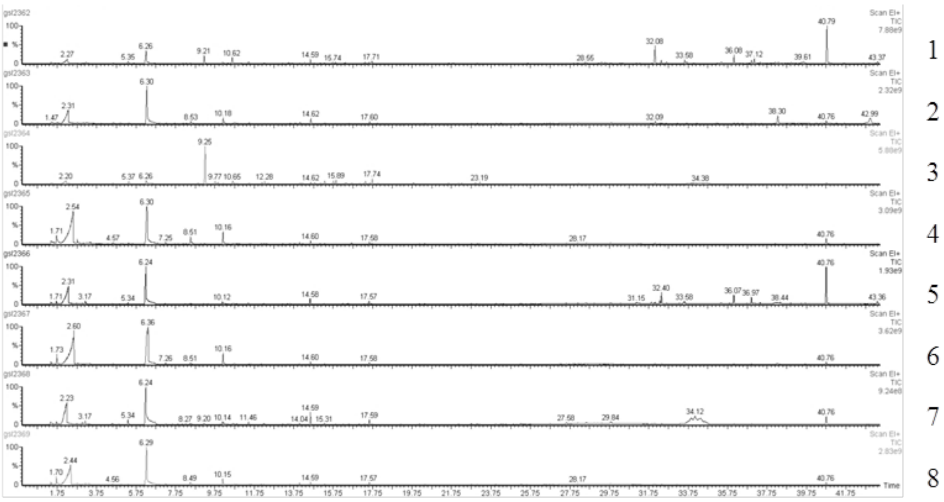

Figure 4: Chromatograms of volatile analyses for treated and untreated materials

Table 1: Overview of difference in terpene occurrence between untreated and Firmolin™ modified samples

Compound	(1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)
α-pinene	✓	×	✓	×	×	×	✓	×
camphene	×	×	✓	×	×	×	×	×
β-pinene	✓	×	✓	×	×	×	×	×
o- or *m*-cymene	×	×	✓	×	×	×	×	×
limonene	✓	×	✓	×	×	×	×	×
fenchol	✓	×	×	×	×	×	×	×
α-campholenal	✓	×	✓	×	×	×	✓	×
pinocarveol	✓	×	×	×	×	×	×	×
cis-verbenol	✓	×	✓	×	×	×	×	×
pinocarvone	✓	×	×	×	×	×	×	×
myrtenal	✓	×	✓	×	×	×	×	×
verbenone	✓	×	✓	×	×	×	×	×
2-camphanol acetate	×	×	✓	×	×	×	×	×
β-parasinsene	×	×	✓	×	×	×	×	×
junipene	×	×	✓	×	×	×	×	×

For the softwoods, it is interesting to observe the significant increase in furfural (peak around 6.3 minutes), resulting from the fragmentation of pentosan within the hemicellulosic component and subsequent ring reduction (Figure 5). There was also an increase in the peak corresponding to 5-methylfurfural (10.15 minutes approx.)

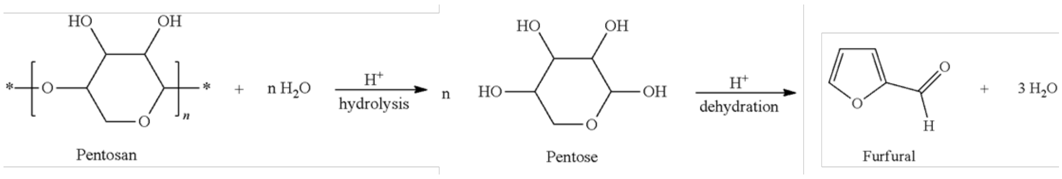

Figure 5: Formation of furfural from pentosans

FT-IR analysis

The spectra for Norway spruce showed slight changes in selected signals as a result of the thermal treatment. The C=O stretching vibrations from acetyl, carbonyl and carboxyl groups at 1735 cm^{-1} was reduced as a result of the thermal treatment (Figure 6a), with an increase in a new peak at a lower wavelength around 1710 cm^{-1}, which is in agreement with a similar study on lime (Popescu *et al*., 2013). There was also a small migration of the peak at 1032 cm^{-1}(C-O deformation in aliphatic alcohols and ethers) to a lower wavelength and the peaks at 898 cm^{-1} (pyranose ring) and 812 cm^{-1} (lignin vibration), respectively, were more pronounced (Figure 6b). The spectra of radiata pine showed a similar decrease in the peak at 1734 cm^{-1}, with the emergence of another peak at 1706 cm^{-1}, whilst the change in the characteristic peak for beech was from 1735 cm^{-1} to 1715 cm^{-1}and for obeche 1735 cm^{-1} to 1708 cm^{-1}. For obeche, there was also a significant peak reduction at around 1650 cm^{-1}, which may be attributed to a reduction in the C=C *cis* stretching of unsaturated acids or sterols present within tannins (Sun and Tomkinson 2002).

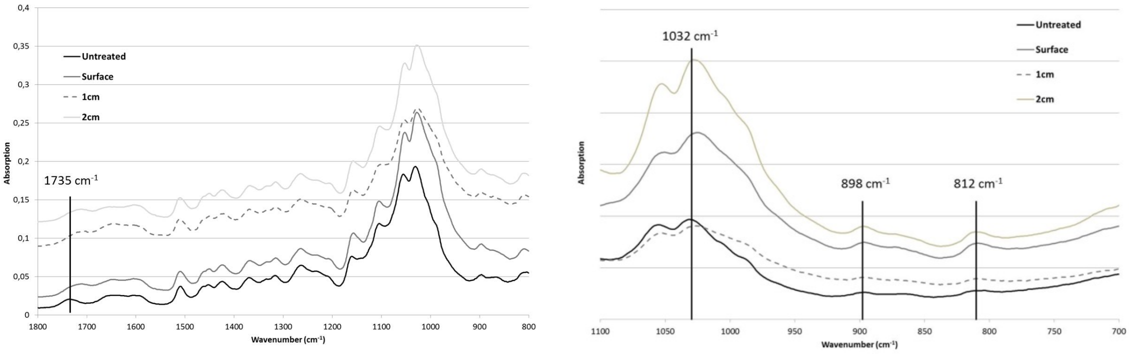

Figure 6: Depth profile FT-IR spectra of Norway spruce (a) between 1800-800 cm^{-1}, (b) closer examination at peaks between 1100-700 cm^{-1}

In the case of spruce, evaluation of the inter- and intra-molecular hydrogen bonding at around 3350 cm^{-1} showed slight progression of the convoluted peak to a lower wavelength, again matching previous observations (Popescu *et al*. 2013).

SEM analysis

The microstructures of the thermally modified materials were compared to their unmodified counterpart regarding visible changes in the cross-sections. For the blocks there samples were also taken from different depths from the surface. The boards of radiata pine and obeche showed no visible changes in the microstructure between unmodified and thermally modified samples (see Figure 7 for unmodified and modified radiata pine microstructures). The spruce boards showed some cell wall fragmentation in the earlywood. However it is hard to conclude whether the damage was done during modification or initial handling and drying since there was also cell wall damage in the earlywood of the unmodified spruce sample. The blocks of thermally modified beech and spruce showed no differences in microstructure between the surface and inner part – this is in agreement with the FT-IR results where very little difference was found. Figure 8 shows the microstructure of unmodified and thermally modified spruce boards.

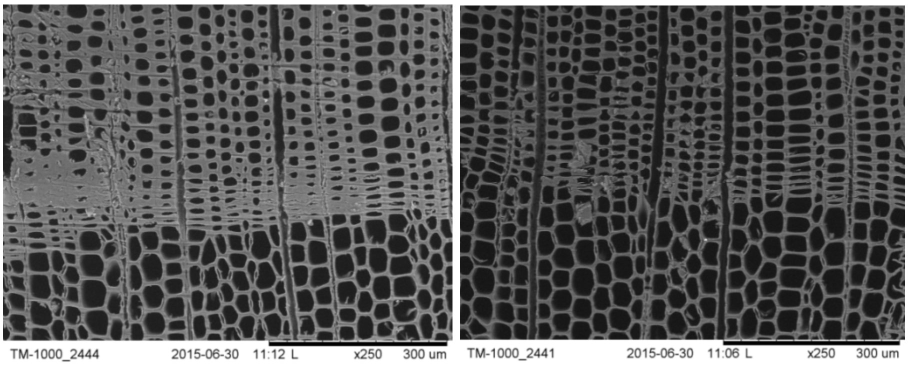

Figure 7: Micrographs of unmodified (left) and thermally modified (right) radiata pine

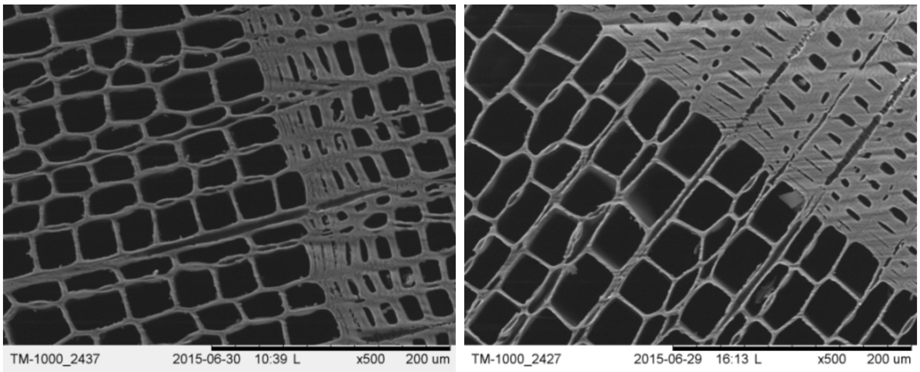

Figure 8: Micrographs of unmodified (left) and thermally modified (right) spruce blocks

CONCLUSIONS

Firmolin™ represents a process that has already been commercialised. The results from this study confirm that there appears to be uniform treatment throughout the modified samples. There is some evidence of the cell wall fragmentation that is often noted with more aggressive thermal modification processes. The EMC of modified spruce was found to be lower than that of radiata pine, which will be substantiated in further studies. As with all thermal processes, there was removal of most of the volatile organics present, which could partly contribute to some of the small changes noted in the FTIR analyses.

ACKNOWLEDGEMENTS

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SESSION SIX

Evaluation of Properties

Weathering Stability of PF-treated Veneer Products from Beech Wood

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Keywords: beech, cracking, field test, phenol modification, veneer, weathering stability

ABSTRACT

This work deals with an evaluation of the weathering stability of Laminated Veneer Lumber made of phenol formaldehyde (PF) modified beech *(Fagus sylvatica)* veneers. It is known that cell wall modification with low molecular weight PF can bring dimensional stability to wood and increase the resistance to fungal attack, but phenol as well as lignin can be degraded by UV-light. However, the benefits from PF-modification seem to increase the weathering performance. To estimate this effect a field test and an artificial laboratory test were performed. Both tests focussed on the dimensional stability, water uptake and crack performance. For the production of the samples different impregnation resins were used at varying concentrations. The impregnation was done in an autoclave under vacuum and subsequent overpressure. For the board production different pressing parameters were set which led to different raw densities. The performance of samples with a relatively low resin loading and low densification were of special interest. The samples were exposed to the weathering tests without a coating. Whereas the laboratory test lasted 5 weeks, the field test was planned for 3 years and is therefore yielding intermediate results after 9 months. Evaluation of the data has shown that PF-treatment gave weathering stability to all of the variants tested. With regard to dimensional stability, the densification in combination with the resin loading had the greatest influence, whereas the resin type played a minor role when proper cell wall penetration was achieved.

INTRODUCTION

The fundamental aim of most wood modification techniques is to improve dimensional stability, resistance to fungal decay and resistance to weathering without the use of biocides. Each kind of wood modification has its own drawbacks and advantages, but its effectiveness always depends on the intended use. The use of phenol formaldehyde to impregnate beech veneers is a long-known method to protect plywood against fast wetting (Stamm *et al.* 1938, 1942, 1955, Stamm 1939) and to improve weathering stability (Evans *et al.* 2013). Our own studies (Bicke *et al.* 2012), as well as those of Furuno *et al.* (2004), indicate good resistance to fungal attack if alkaline low molecular weight phenolic resins are used. If the molecules are small enough, they are able to penetrate sufficiently into the cell wall rather than just filling the cell lumens. For the resin to be evenly distributed throughout the wood, a full cell impregnation process in an autoclave is known to be a suitable way. However Bicke and Militz (2014) reported that a submersion process in combination with wet storage could result in the same WPG, if solutions with higher concentration were used.

Earlier work with the same material showed excellent results for the durability and good mechanical properties. Therefore, the approach of this work was to investigate how

LVL from PF-modified beech veneers behaves under natural weathering conditions and if a short term lab test is suitable to give an idea about the dimensional stability under varying climates. The evaluation therefore focussed on non UV-light dependent properties, such as swelling and water uptake – the assessment of cracking and an estimation of the colour change completed the work.

EXPERIMENTAL

For the production of the LVL, rotary cut beech veneers were modified with a variety of low molecular weight PF impregnation resins - later indicated with a capital letter for each resin type. To achieve different WPG, the concentration of PF in water was varied from 12.5% - 55% PF solids. Impregnation of the 3.7mm thick veneers was done in an autoclave under vacuum and subsequent overpressure. Before gluing with a standard PF adhesive, drying was carried out to reach suitable moisture contents. For board production, 8 plies were assembled with the majority of the veneers oriented with the grain parallel to the axis of the panel with the second and the seventh veneers oriented perpendicular to this. To achieve different levels of densification, a normal and a high pressing pressure was used, which led to different densities. The pressing temperature and the duration were always the same. After forming the boards the samples for the tests were cut without sanding. The samples for the accelerated weathering test measured 100mm in width and 400mm in length. The thickness was determined by densification – varying from 30mm to 25mm. The samples for the natural weathering instead measured 440mm, so that any bending would be more easily traceable. For both tests the samples were exposed without any coating or other surface treatment. The lab test lasted 5 weeks, the field test was planned as a 3-year test and intermediate results after 9 months are presented. The lab test was a house standard which consisted of 3 phases per micro cycle. First phase was a water spray, the second phase was conditioning and the third phase was IR- and UV-light irradiation. The micro cycle was repeated five times and with two days in a fridge, this formed the macro cycle which took one week. The orientation of the samples was nearly horizontal, with an inclination of 2.5% (2.25°). The overhead irrigation and irradiation impinged vertically on the surface of the sample. Figure 1 illustrates the weathering micro cycles.

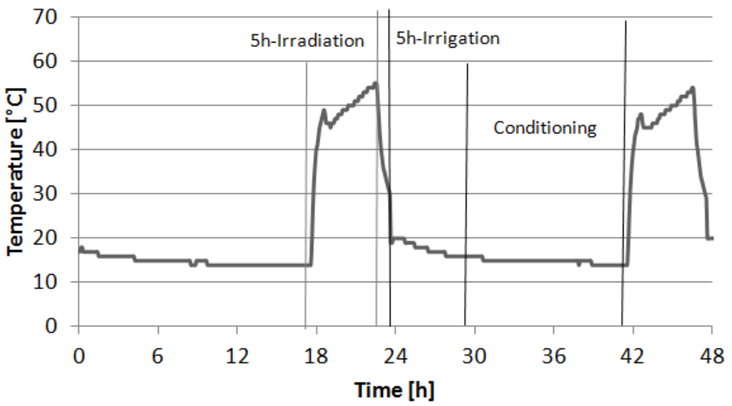

Figure 1: Micro cycles at the accelerated lab weathering test

Every week (cycle), the weight and the dimensions of the samples were measured and both sides of the sample were scanned on a calibrated photo scanner. An evaluation of the cracks was carried out in accordance with a standard for the assessment of coating defects (DIN ISO 4628-4; Table 1). The position of the sample was systematically changed to avoid any influence of the sample position.

Table 1: Specific values for the assessment of surface defects

Value	Number of Cracks	Value	With of Cracks
0	not any visible cracks	0	not any visible cracks with magnification of 10
1	single beginning cracks	1	single beginning cracks with magnification of 10
2	few cracks, clearly visible	2	beginning cracks visible by eye
3	moderate numerous cracks	3	cracks clearly visible by eye
4	plenty of cracks	4	crack width < 1 mm
5	very many cracks	5	crack width > 1 mm

In the natural weathering test the samples were placed on racks in an inclined position of 45°C facing south. They were evaluated every three months for the same parameters as for the lab test, but in addition the bending / deformation of the sample was measured.

RESULTS AND DISCUSSION

The production of LVL-boards from PF-impregnated and dried beech veneers with different WPG and pressing pressure consequently led to a variety of raw basic densities (Table 2). Since phenol acts as a softening agent (Gabrielli and Kamke 2010), the PF-modified boards were densified by the increased pressures in the hot press, whereas the untreated boards were only influenced a little.

Table 2: Raw Densities (kg/m^3) of PF-modified beech LVL weathering test samples given as mean values for two pressing pressures.

Resin	**R**	**A**	**A**	**B**	**C**	**D**	**E**	**D**	**A**	**B**	**C**	**E**
WPG [%]	**0**	**15**	**30**	**30**	**30**	**30**	**30**	**48**	**60**	**60**	**60**	**60**
2 N/mm²	732	790	814	868	884	924	846	1052	1015	1009	1011	1063
STD	22	69	2	15	14	11	9	30	3	51	8	16
6 N/mm²	843	1039	1157	1187	1221	1164	1140	1294	1214	1290	1286	1263
STD	2	9	34	7	5	30	57	34	60	65	37	7

The weights measured in the accelerated weathering test culminated in the fifth week and only the final values are displayed in Figure 2. The reference boards took up more than 30% of the initial weight, which was the weight at equilibrium at 20°C and 65% RH (EMC~10%). The variant with 15% WPG showed a small reduction in uptake for the lower pressing pressure without densification. At the higher pressure and densification it was reduced by more than two thirds. For the variant with a WPG of 30%, except for resin type D, all the values for the un-densified boards were below 10% and for densified boards below 5%. At a WPG of 60% the maximum uptake was 5.5% for the un-densified and 1.5% for the densified series. During the nine months of the natural weathering test (***Figure***b) very similar results were found for the water uptake, except the reference and the variant with 15% WPG, which were not as wet.

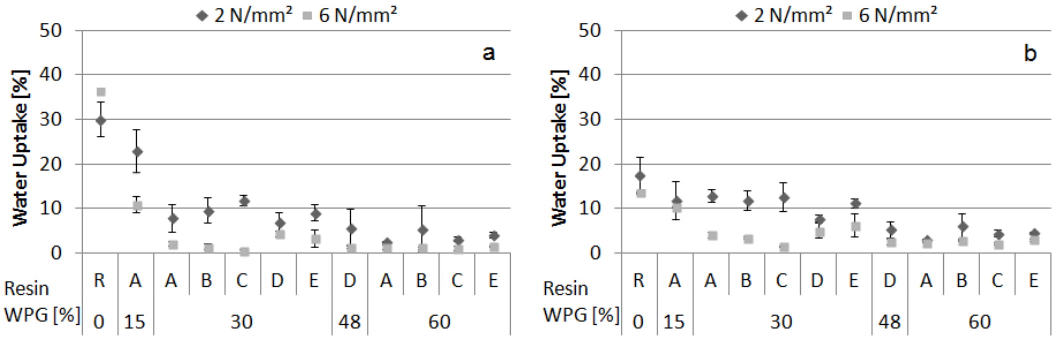

Figure 2: Water uptake of PF-modified LVL within 5 weeks at the accelerated weathering test (a) and within 9 months at the natural weathering test (b)

As Table 2 shows, the boards increased in density with WPG and pressing pressure – a point plot of both density and water uptake for the treated boards only gave the obvious negative correlation. This showed the effect of WPG alone in case of the lower pressure and the effect of densification in the case of higher pressure. It also becomes clear that the same reduction in uptake can be achieved by densification as with loading with resin.

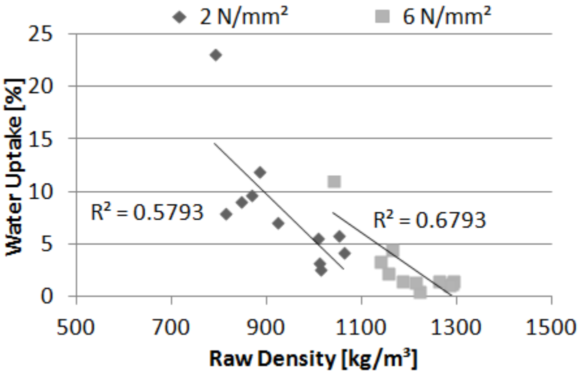

Figure 3: Correlation of water uptake and density for PF-modified beech LVL at the accelerated weathering test

The results for radial swelling in the lab test (Figure 4a) and during natural weathering (Figure 4b) appeared to follow the trends for the water uptake. For the reference series and the 15%WPG treatment, higher swelling could be observed in the lab test, which accords with the greater water uptake observed, compared to the field test.

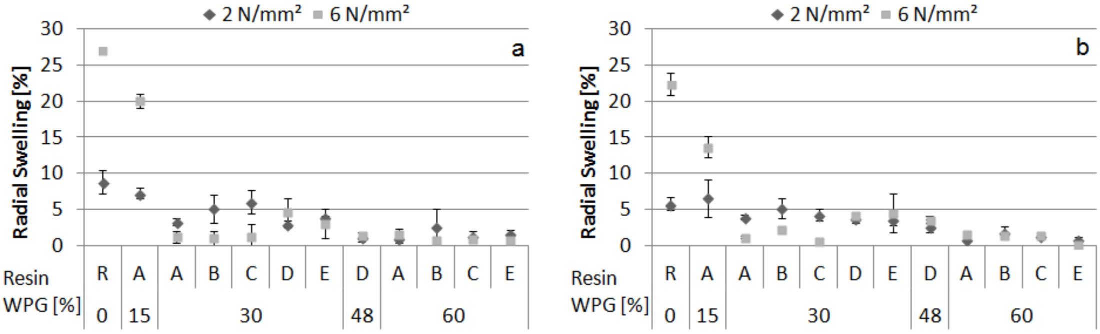

Figure 4: Radial (thickness) Swelling of PF-modified LVL within 5 weeks at the accelerated weathering test (a) and within 9 months at the natural weathering test (b)

It has to be noted that for WPGs above 30% the swelling rate is reduced by pressure and thus the degree of densification. The opposite was true for the reference and the 15% WPG, where the swelling was higher with the higher densification. This indicates that compression is only sufficiently fixed at higher WPG and under these conditions could reduce the swelling rate. Figure 5 shows the correlation between swelling rate obtained in the natural weathering and lab tests as a point plot which proves the high correlation of results from the two different tests.

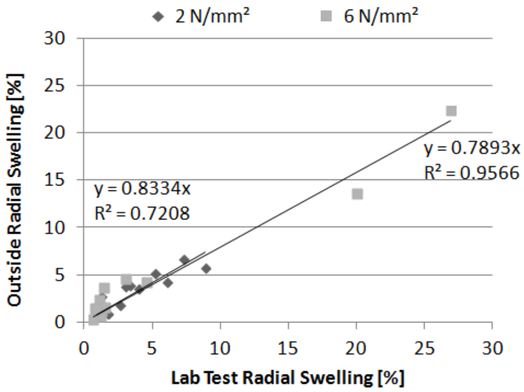

Figure 5: Correlation between natural weathering and accelerated weathering at lab scale results for the swelling in radial wood direction

In contrast to the swelling and water uptake tests, the correlation between the lab test and natural weathering was very poor for the number of cracks (Table 3). For p=2N/mm², the reference and the 15% WPG series acquired very many cracks in the natural field test, however in the lab they performed better. For the treated series with a WPG of 30% the number of cracks was found to be moderate in both tests - hence a slight reduction in the number of cracks was concluded. With 60% WPG the results appeared to be more controversial, with plenty of cracks in the lab test and both high and low values in the natural weathering. The difference between both tests became more severe, indicating that the variation of results was problematic, in the case of the reference and 15% WPG series at higher pressure (6 N/mm²). At the same pressure, the series with 30% and 60% WPG showed a similar mean value of 3 for both tests and indicate therefore a slight reduction of cracks by the treatment.

Table 3: Specific values for the number of cracks as arithmetical means

Pressure	**Resin**	**R**	**A**	**A**	**B**	**C**	**D**	**E**	**D**	**A**	**B**	**C**	**E**
[N/mm²]	**WPG [%]**	**0**	**15**	**30**	**30**	**30**	**30**	**30**	**48**	**60**	**60**	**60**	**60**
2	**5 weeks**	4	3	3	1	3	3	2	4	4	4	4	4
	STD	0.8	2.8	0.0	0.0	1.5	0.0	1.0	0.7	0.0	0.7	0.6	0.0
	9 months	5	5	2	3	3	3	3	3	3	4	2	2
	STD	0.0	0.0	0.0	0.0	0.7	0.0	0.7	0.7	1.4	0.0	0.0	1.4
6	**5 weeks**	3	1	3	3	3	2	2	3	3	4	4	3
	STD	0.0	0.0	0.0	1.4	1.4	1.0	1.0	1.4	1.3	0.0	0.6	0.7
	9 months	5	4	3	3	3	1	3	2	4	4	4	3
	STD	0.0	0.7	2.1	0.0	1.4	1.4	1.5	0.7	0.6	0.0	0.7	0.7

The evaluation of the width of the cracks (Table 4) indicated that without densification nearly all results, except for the 60% series, were similar at the lower pressure in both the lab test and in natural weathering. They ranged between 2 and 3 and showed initial and clearly visible cracks of less than 1 mm. The 60% WPG series at the same pressure showed more cracks at the initial stage in the natural weathering and were therefore ranked better. For the densified series all of them except for the reference performed one class better in the natural weathering than in the lab test, but in the end the overall variation was higher in the natural weathering test.

Table 4: Specific values for the width of cracks given as arithmetical means

Pressure	**Resin**	**R**	**A**	**A**	**B**	**C**	**D**	**E**	**D**	**A**	**B**	**C**	**E**
[N/mm²]	**WPG [%]**	**0**	**15**	**30**	**30**	**30**	**30**	**30**	**48**	**60**	**60**	**60**	**60**
2	**5 weeks**	3	3	3	3	3	3	2	3	3	3	2	2
	STD	0.5	0.0	0.7	0.0	0.0	0.0	0.5	0.0	0.7	0.0	0.0	0.0
	9 months	3	3	2	3	3	3	3	3	3	2	2	2
	STD	0.8	0.0	0.0	0.7	0.7	0.7	0.7	0.0	0.7	0.0	0.0	0.0
6	**5 weeks**	3	3	2	2	3	3	2	4	3	3	2	3
	STD	0.0	0.0	0.0	0.0	0.0	0.0	0.5	0.7	0.5	0.0	0.6	0.0
	9 months	3	3	2	2	2	2	2	4	2	2	3	2
	STD	0.0	0.0	0.0	0.0	0.0	2.1	0.5	0.7	0.6	0.0	0.7	0.0

The bending or deflection of the specimen was measured, but they remained straight and in all cases it was less than 1% on basis of half of the length of the sample. The variance therefore was higher than the difference between the groups.

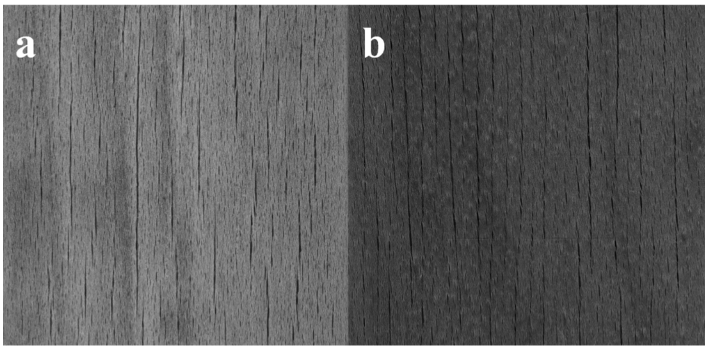

Figure 6: Reference samples after 9 months of natural weathering (a) and after 5 weeks of accelerated weathering (b)

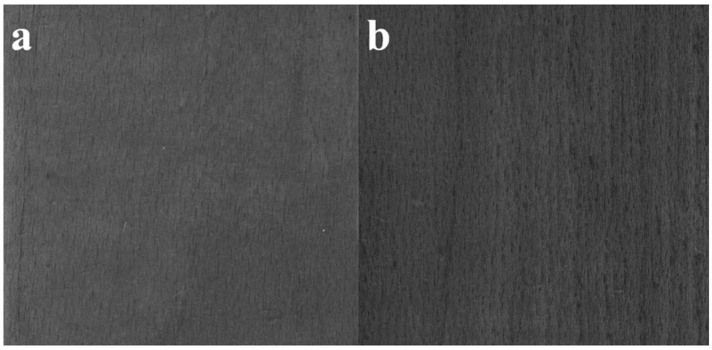

Figure 7: Samples from treated veneers with resin type A, 30% WPG and compressed under 6 N/mm² after 9 months of natural weathering (a) and after 5 weeks of accelerated weathering (b)

Figure 6 and Figure 7 demonstrate that generally the longer time and intensity of UV light in combination with rainfall and washout during natural weathering (a) brightened the samples. The treated series indeed showed a very late onset of greying, compared to the reference which turned grey more quickly. Anyhow, greying had also started after 9 months in the treated series. In contrast the lower intensity and time of UV light in the lab test only darkened untreated as well as the treated samples.

CONCLUSIONS

Beech veneer products, especially LVL, can benefit from PF-Modification. All series which gained a WPG of 30% performed very well in the weathering tests, and densified and undensified were very close. The boards with a WPG of 60% obviously showed the best results for water uptake and swelling, but those advantages could not overcome their disadvantages, as they where the heaviest and extremely resource wasting variants. For the production process of the boards, it can be concluded that the pressing pressure strongly influences the density of PF-treated boards, whereas the untreated veneers undergo only very little densification. The water uptake showed then a negative correlation with the raw density of the PF-modified boards; whereas the 15% WPG was far away from the linear regression model. The significantly higher swelling of the untreated boards with only little densification was due to a spring back effect. These findings indicated that densification only in combination with a minimum WPG of 30% significantly reduces water uptake and swelling in the radial direction. The series which gained 30% WPG showed some variation between the resin types, but under these conditions this seemed to be negligible. These findings are therefore a good complement to small scale laboratory tests on dimensional stability with solid wood. Finally, both the weathering tests performed were appropriate to give answers to the improvement of beech LVL by PF-modification with regard to dimensional stability under weathering conditions.

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Evaluating the Optimisation of Wood Modification with Polybutylene Succinate Bio-Polyester

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Keywords: bio-polyester, impregnation, polybutylene succinate, wood modification

ABSTRACT

In this paper, the optimisation attempts of wood chemical modification with polybutylene succinate oligomers (OBS) are reported. The heating duration as well as the temperature of the OBS impregnated samples was found to be, logically, essential. Extensive heating steps of 2 days and 9 days were carried out at 160°C after impregnation. The longer the samples are heated, the higher the $ASE^{*}_{95\%RH}$ values: 44% and 55% for 2 days and 9 days treatments, respectively. Not only do these two parameters influence the treatment efficiency. It appears that the relative humidity during treatment and the wood moisture content before impregnation play a significant role in the wood treatment efficiency as well: samples subjected to water soaking at room temperature after treatment and samples impregnated at a high equilibrium moisture content lead to $ASE^{*}_{95\%RH}$ of 55% as well.

INTRODUCTION

Promising wood modification techniques using various biopolymers, such as lactic acid (LA) and polybutylene succinate (OBS) in their oligomeric form, via bulk impregnation and in-situ polymerization has already been reported (Noël *et al*. 2014, 2015a, 2015b, Vitkeviciute 2015). The following phenomenon was observed and will be described in this paper (Figure 1).

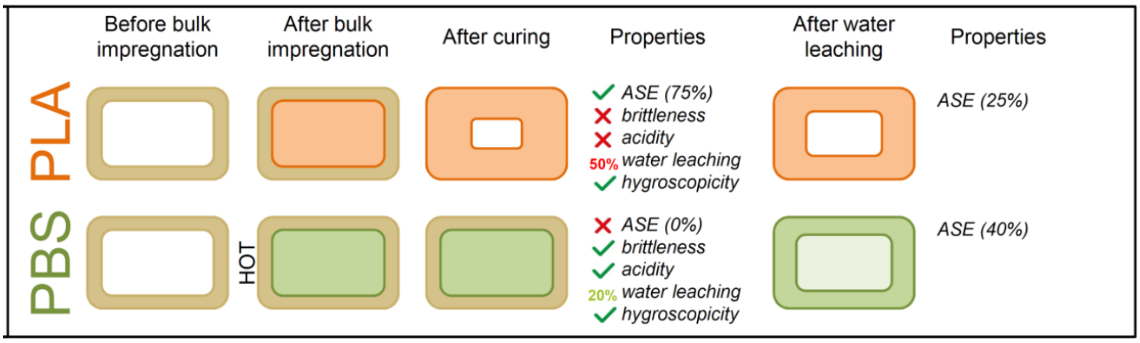

Figure 1: Comparison of PLA and PBS oligomers efficiency for wood modification in relation to the cell wall modification

While LA based treatments were revealed to be bulking the cell wall, PBS remained lumen-filling only. The former lead to very good dimensional stabilisation, with an anti-swelling efficiency (ASE) of up to 75% under certain conditions, but brittleness increased, while the latter decreased the hygroscopicity of wood but could provide only limited dimensional stabilisation. On the other hand, the OBS lumen filling treatments did not affect the mechanical properties at all, whether the samples had been leached or not, and the oligomers retention into wood structure was even higher after water leaching: only 20% of polymer loss. The $ASE^*_{95\%RH}$ was logically non-existent, as the cell walls were not impregnated.

It has been noticed, however, that placing OBS treated samples in water for the leaching resistance evaluation allowed a substantial increase in properties, evidenced by high $ASE^*_{95\%RH}$ values and no impact on the mechanical performance (Noël et al., 2014). For this reason, OBS treatment optimisation was considered promising regarding two treatment conditions: temperature and duration on the one side, which should increase the in-situ polymerisation rate, and water or moisture on the other side for the treatment penetration into wood cell wall.

EXPERIMENTAL

Synthesis of the PBS oligomers (OBS)

Oligomeric polyesters were synthesized by their direct polymerization under vacuum, using a four-necked flask fitted with a magnetic stirrer and reflux condenser linked to an inline cold trap and vacuum pump. Thermometers were used to monitor the polymerization, condenser head, and heater temperatures.

Oligoesters (OBS) were synthesized by melt polymerization of dimethyl succinate and 1,4-butanediol. This was achieved by adding a 25% stoichiometric excess of 1,4-butanediol in the presence of titanium (IV) butoxide as the esterification catalyst. A mixture of dimethylester, 1,4-butanediol, and catalyst was poured into the flask under a nitrogen purge. The mixture was gradually heated to 180°C over 130 min under reduced pressure (150 mbar). At the end of the reaction, oligomers were poured into bottles, sealed and cooled. OBS solidify as a white block when cooled. The melt temperature of OBS was rheologically measured at ca. 75°C.

Wood treatment

Wood samples were immersed in the liquid oligomers at 90°C. The containers were then placed in a vacuum oven under reduced pressure (580 mmHg) for 1 to 2 h, then atmospheric pressure over 1 to 2 h.

The impregnated samples were then wiped and set on aluminium foil in a ventilated oven under certain conditions of temperature and duration which will be always defined in the following. The anhydrous sample weight was measured before impregnation, after impregnation and after heat treatment. Weight uptake was calculated according to Eqn. 1.

$$WU_{i/t}(\%) = \frac{w_{i/t} - w_0}{w_0} \times 100 \qquad (1)$$

where w_i stands for the impregnated sample weight, w_t for the sample weight after complete treatment, and w_0 the oven dried sample weight before treatment.

Anti-swelling efficiency

All treated samples (15x15x10 mm, TxRxL) were placed in 95% relative humidity (RH). The samples dimensions were measured before exposure in the dry state (due to the treatment process) and after weight stabilisation. Regular weight measurements were made in order to determine the equilibrium moisture content of samples with time.
As some treatments show a strong bulking effect in the cell wall, whereas others only penetrate the wood lumens, the ASE calculation was based on the corrected swelling calculation of treated samples (St) as defined in Eqn. 2 (Thybring 2013):

$$S_t^* \ (\%) = \frac{V_{95\%st} - V_t}{V_0} \times 100 \tag{2}$$

$$ASE^* \ (\%) = \frac{S_{nt} - S_t^*}{S_{nt}} \times 100 \tag{3}$$

where $V_{95\%st}$ stands for the treated sample volume after stabilisation at 95%RH, V_t for the treated sample volume before stabilisation at 95%RH, V_0 the oven dried sample volume before treatment and S_{nt} the swelling of the untreated reference sample:

$$S_{nt} \ (\%) = \frac{V_{95\%snt} - V_{nt}}{V_{nt0}} \times 100 \tag{4}$$

where $V_{95\%snt}$ stands for the volume of the untreated reference sample after stabilisation at 95%RH and V_{nt} for the oven dried volume of the untreated reference sample.

For the treated samples, the reduced equilibrium moisture content EMC_{Rt} was calculated as defined in Eqn. 5:

$$EMC_{Rt} \ (\%) = \frac{w_{95\%st} - w_t}{w_0} \times 100 \tag{5}$$

where $w_{95\%st}$ stands for the treated sample weight after stabilisation at 95%RH, w_t for the treated sample weight before stabilisation at 95%RH, and w_0 the oven dried sample weight before treatment.
The swelling and anti-swelling efficiency of samples soaked in liquid water were calculated as well according to formulae (2), (3) and (4) where “95%” can be replaced by “lw” standing for liquid water.

Leaching

The treatment resistance to water leaching was measured in terms of weight loss of polymer (WLP) resulting from the ASE test in liquid water. The samples were soaked in water at 23°C for 7 days. At the end of the test, the samples were air dried at 23°C / 56%RH for 24h and subsequently oven dried until constant weight. The WLP was calculated as defined in Eqn. 6:

$$WPL \ (\%) = \frac{w_{tl0} - w_t}{w_t - w_0} \times 100 \tag{6}$$

where w_{tl0} stands for the treated sample weight after leaching and oven drying, w_t for the treated sample weight (necessarily oven dried) and w_0 the oven dried sample weight before any treatment.

Dynamic mechanical Analysis

DMTA analysis was carried out on a Triton TTDMA equipped with a humidity box allowing the set-up of a temperature ramp and RH in the chamber, on samples of dimensions 50x10x4 mm (LxRTxTR). The temperature changes were manually performed when the conditions in the chamber are stable. Once the temperature and RH were stable, the average of the five last values of the stabilized storage modulus values, taken at 3 min intervals, was calculated and stands as the storage modulus value reported in Figure 3. Only thermal scans carried out at 1 Hz are reported in this paper.

RESULTS AND DISCUSSION

Performance of OBS treatment and influence of subsequent water leaching

The combination of OBS impregnation with long dry heat treatment (9 days at 160°C) appeared to lead to very good performance ($ASE^*_{95\%RH}$ up to 55%) even with no cell wall chemical modification. Besides, when the impregnation was followed by simple drying/curing at moderate temperature (120/140°C) but no further extended heat treatment, it was observed that soaking such OBS treated samples in water for a certain time allowed the partial penetration of the oligomers into wood cell walls, evidenced by the resulting samples swelling after leaching and drying. In that case, the treated samples displayed better dimensional stability ($ASE^*_{95\%RH}$ of ca. 40%) after the water leaching stage than before ($ASE^*_{95\%RH}$ of ca. 30%). Moreover, the severe water leaching period could not extract more than 20% of the impregnated polymer.

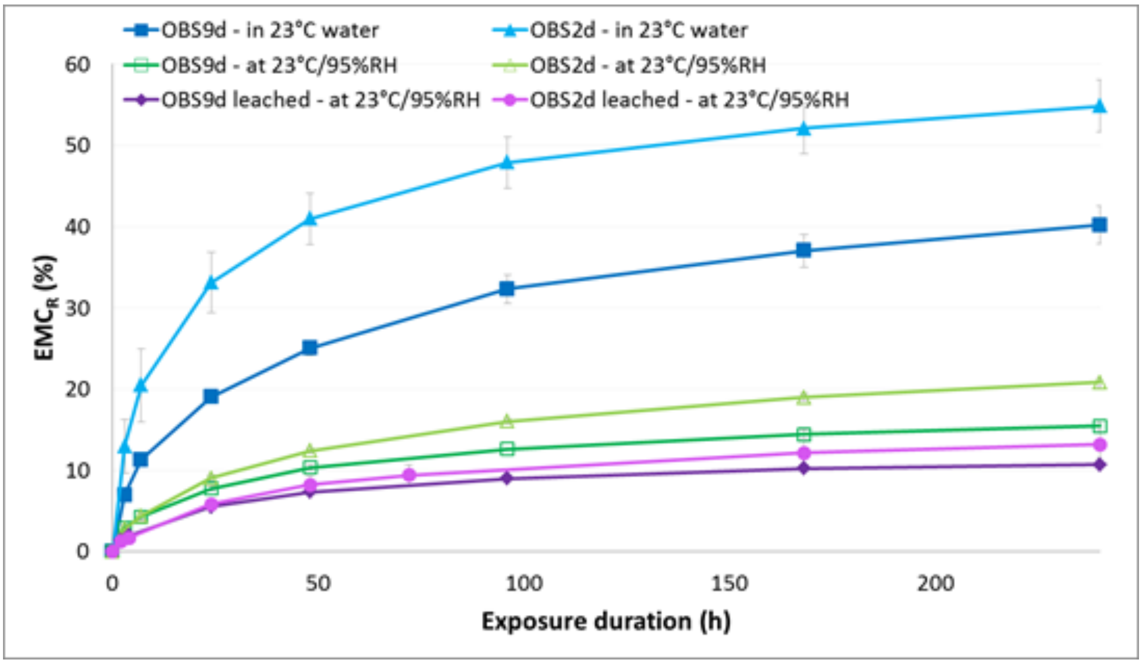

Figure 2: EMC_R of OBS treated samples (160°C/2days and 9 days) along exposure time to 95%RH at 23°C, or to water soaking

The EMC_R of OBS treated samples cured for 2 days or 9 days at 160°C exposed to 95%RH at 23°C are displayed in Figure 2 (green curves). Samples treated in the same way have been exposed first to a water soaking period of 24 days (EMC_R displayed in Figure 2 only up to 240 h, blue curves) and further exposed to 95%RH at 23°C after intermediate oven drying (pink curves). The influence of the treatment duration and water leaching is obvious: after stabilisation, the EMC_R in water of OBS9d is 36% lower than the EMC_R in water of OBS2d; the EMC_R at 95%RH of OBS9d is 36% lower than the EMC_R at 95%RH of OBS2d; and moreover, the EMC_R 95%RH of OBS2d after water leaching is 58% lower than the EMC_R at 95%RH of OBS2d when not subjected to water leaching (44% lower for OBS9d samples).

Because the water soaking of the OBS treated samples lead to significant swelling (up to 13%) after oven drying, the partial penetration of oligomers into the cell wall was assumed. In order to understand this phenomenon better, OBS impregnated samples were subjected to an increase in temperature under stable relative humidity of 35%RH, 57%RH and 86%RH in a three-point bending DMTA set-up. The storage modulus (E’) according to temperature is reported in Figure 3.

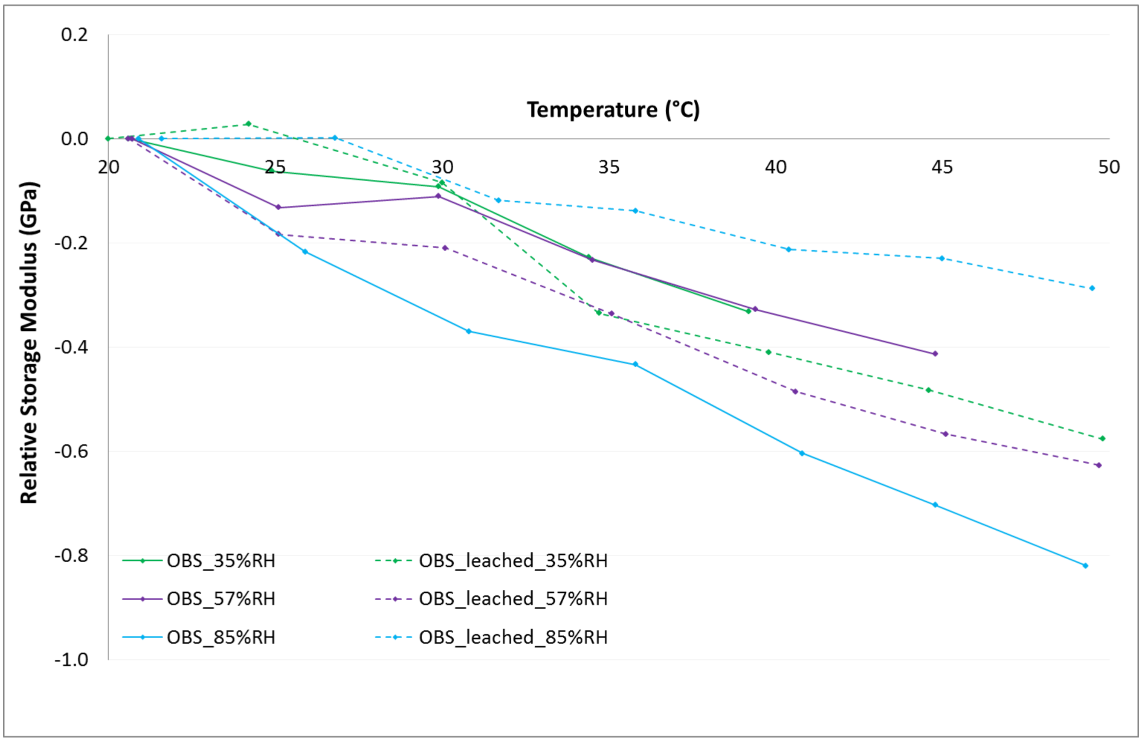

Figure 3: Relative storage modulus of samples not treated, impregnated, impregnated and leached; at 35%RH, 57%RH and 85%RH along temperature increase from 20 to 50°C

The OBS treated samples show interesting behaviour. At 35%RH, the decrease in E’ is regular, except for a slight inflection at 25°C. At 57%RH, the sample behaviour is very similar, with a similar slope after 30°C, except that the inflection at 25°C is more pronounced. The DMTA run has induced the swelling of the OBS samples at 35%RH and 57%RH: 5.6% and 7.4% respectively (swelling measured as the ratio between the sample volume after DMTA run and further oven drying and the sample volume right after hot impregnation of dry samples). At 85%RH, the loss in E’ of the OBS sample is bigger and faster, and the resulting swelling is 17.6%.

The volume control indicates that the DMTA run allowed the polymer to penetrate into the cell wall in the three cases: the higher the RH, the bigger the swelling. This relation between the E' change and the polymer penetration in the cell wall will have to be further studied and could be of great help to better understand the interaction between wood and OBS.

The case of the samples impregnated and leached is different, as the polymer did penetrate into the cell wall during leaching (ca. 10% swelling due to leaching for those samples) and will impact the E' behaviour. At 35%RH, the loss in E' is quite similar to the E' of the impregnated sample, except that there is no inflection at low temperature and that the decrease in E' is a little bit bigger. An additional swelling of 2.4% was measured after the DMTA run (the ratio of the oven dried volume after the DMTA run to the oven dried volume after impregnation and leaching). At 57%RH, the E' curve is very similar to the impregnated sample, with a corresponding inflection at 25°C and a similar slope, however with a bigger decrease. The additional swelling was measured to be 1.7%. At 85%RH, the leached sample behaved differently and showed a very similar change in E' to the reference untreated sample (not presented here). No inflection point is observed and the decrease in E' is very moderate. The additional swelling is 3.7%.

Replication of the water leaching effect in the treatment process

The following sample variants were produced and evaluated in order to conclude the efficiency of the different treatments (Table 1):

Table 1: Treatment parameters evaluated

Ref.	EMC[a] [%]	Impregnation temperature [°C]	Wet step	Dry step
1	0	90	-	Oven heating, 103°C/12h
2	0	90	Water leaching, 23°C/7d	Oven heating, 103°C/2.5d
3	0	90	-	Oven heating, 140°C/12h
4	0	130	-	Oven heating, 103°C/12h
5	0	130	-	Oven heating, 140°C/12h
6	0	90	Wet heating, 100°C/100%RH/30min	-
7	0	90	Wet heating, 100°C/100%RH/30min	Oven heating, 103°C/4d
8	98[b]	90	-	Oven heating, 103°C/4d

[a]Wood EMC before impregnation, [b]Non dried wood, freshly cut

To characterize the treatment efficiency, the ASE in liquid water (23°C/7d) was first measured (ASE^{*}_{lw}). After the soaking period in water, the samples were oven dried at 103°C until constant weight and subjected to the ASE measurement at 95%RH/23°C. The treatment influences the physical properties of wood and their efficiencies are reported in Table 2.

Even when carried out at different temperatures and on samples of different EMC, there was never any swelling induced by the impregnation step (S_i). Yet a high weight uptake (WU_i) was measured in all cases (ca. 65%) except for the variant 8. In this case, there was no swelling nor weight uptake observed. This is most likely because the free water, and maybe partially the bound water, was replaced by the oligomers. This impregnation induced a clear and intense foaming which corroborates the hypothesis. Only a few treatments induced the samples to swell (S_t): variants 3 and 5 lead to ca. 7% swelling while variants 2, 7 and 8 lead to ca. 13% swelling. Variants 3 and 5 correspond to the high temperature drying step. Variants 2, 7 and 8 imply either a wet step or the treatment of wet wood. Wet heating of 30 min (variant 7) lead to a higher penetration of the oligomers into the cell wall than water leaching at room temperature for 7 days (variant 2). The higher the swelling during treatment (S_t), the more reduced the treatment weight uptake (WU_t). Variants 2, 7 and 8 might have provoked the partial hydrolysis of the oligomers allowing penetration into the cell wall and a partial release of the oligomers from the wood at the same time.

Table 2: Treatments description and efficiency

Ref.	S_i [%]	WU_i [%]	S_t[a] [%]	WU_t[a] [%]	ASE^*_{lw}[b] [%]	EMC_{Rlw}[b] [%]	**WLP** [%]	S_{lw}[c] [%]	$ASE^*_{95\%}$[d] [%]	$EMC_{R95\%}$[d] [%]
1	0.2	66.6	0.9	64.6	-1.4	52.6	-23.6	5.6	30.3	31.4
	± 0.4	*± 2.1*	*± 0.3*	*± 2.2*	*± 6.5*	*± 0.8*	*± 0.4*	*± 0.4*	*± 5.8*	*± 0.8*
2	0.3	65.3	11.6	49.6	42.8	56.9	-5.2	2.1	55.2	30.5
	± 0.1	*± 5.4*	*± 0.7*	*± 4.2*	*± 4.4*	*± 1.9*	*± 0.3*	*± 0.3*	*± 5.1*	*± 0.5*
3	-0.1	63.8	7.8	55.2	37.1	53.8	-7.3	-2.1	37.3	28.0
	± 0.3	*± 7.5*	*± 0.3*	*± 6.6*	*± 3.2*	*± 1.3*	*± 0.7*	*± 0.8*	*± 6.3*	*± 0.5*
4	0.5	62.6	0.8	60.8	1.9	55.6	-21.2	5.1	33.2	30.4
	± 0.4	*± 9.5*	*± 0.1*	*± 9.3*	*± 11.9*	*± 2.0*	*± 0.6*	*± 0.7*	*± 11.9*	*± 1.0*
5	0.8	68.2	6.7	63.0	29.3	55.6	-11.7	0.5	40.1	30.5
	± 0.6	*± 5.5*	*± 1.1*	*± 5.1*	*± 9.7*	*± 3.1*	*± 1.0*	*± 1.5*	*± 9.8*	*± 1.3*
6	0.5	64.2	-[e]	-[e]	-[e]	-[e]	-[e]	-[e]	18.3	31.8
	± 0.2	*± 5.5*							*± 7.6*	*± 1.7*
7	0.7	65.2	14.9	51.9	53.8	61.0	-16.4	-1.9	47.8	30.5
	± 0.4	*± 7.4*	*± 1.0*	*± 7.2*	*± 3.8*	*± 0.6*	*± 1.0*	*± 0.8*	*± 7.2*	*± 1.0*
8	-2.4	-1.8	12.0	57.4	56.9	48.0	-19.5	-0.8	55.1	29.4
	± 1.4	*± 0.9*	*± 1.2*	*± 5.5*	*± 4.3*	*± 3.4*	*± 0.9*	*± 0.8*	*± 4.9*	*± 2.1*

[a] Treatments are defined in Table 1. They consist in the wet and dry step. [b] ASE^* and EMC_R in liquid water. [c] Swelling measured after the water leaching and oven drying. [d] ASE^* and EMC_R at 95%RH. [e] This data could not be calculated because the ASE_{lw} step directly followed the wet step. An intermediate drying would have necessary for the calculation.

With quite similar EMC_R in water of ca. 55%, the ASE^* in water strongly depends on the process. Variants 7 and 8 reach the highest ASE^*_{lw} values with ca. 55%. The wet heating and the high EMC of the samples before impregnation are two very efficient processes, better than a soaking period before heating (variant 2). The dry treatments (variants 3 and 5) lead to high ASE^*_{lw} as well because of the high heating temperature. They reveal however that a high *impregnation* temperature does not improve the final properties. This is also observed with variants 1 and 4, showing no efficiency because of a heating temperature that is too low, whether the *impregnation* temperature be high or low.

The loss of polymer (WPL) during the 7 days water leaching was always ca. 20% except for variants 2, 3 and 5. The water leaching carried out as a preliminary wet step before the ASE^*_{lw} test most likely induced a certain loss, which explains the lower WPL measured (variant 2). For variants 3 and 5, the high temperature heating seems to have induced better fixation of the oligomers in the wood. Logically, no additional swelling (S_{lw}) is observed on samples which already swelled during the treatment, and vice versa. Finally, with an EMC_R always close to ca. 30%, the $ASE^*_{95\%}$ reached the highest value of 55% for variants 2 and 8, showing that the water leaching at room temperature or the impregnation of wet wood lead to similar efficiency. The two wet/dry step-treatment (variant 7) was not that efficient. The high temperature heating conferred an $ASE^*_{95\%}$ value of ca. 40%, showing that the temperature is not the most significant parameter in the treatment. Variants 1 and 4 involving no wet step and a low heating temperature reached an $ASE^*_{95\%}$, of only ca 30% while variant 6, with an $ASE^*_{95\%}$ value of 18% only, indicated that the wet step has to be followed by a dry step to confer a high enough efficiency.

CONCLUSIONS

The strong dependence between the OBS oligomers in wood and the relative humidity or moisture content of the wood has been observed and will help in designing an efficient treatment process. The pre-results presented in this paper showed that substantial dimensional stability could be conferred to wood under certain conditions. The phenomenon has not been fully explained yet and will have to be further analysed. For instance, the degree of polymerisation of the oligomers in the different treatment steps will have to be analysed in order to conclude probable hydrolysis of the chains during treatment and/or leaching. Furthermore, the mechanical properties as well as the durability of the treated wood will have to be investigated as well.

Besides, the DMTA analysis provided interesting pre-results and was revealed to be a possible way to investigate the influence of the treatment conditions on the mechanical properties, as well as on the interaction of wood with the biopolymer.

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Life Cycle Assessment as a Tool to Promote Sustainable Thermowood Boards: a Portuguese Case Study

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Keywords: EPD, LCA, PCR, Thermowood

ABSTRACT

The aim of the present work was to conduct a Life Cycle Assessment study of thermally-modified Atlanticwood® pine boards based on real data provided by the Santos & Santos Madeiras company. Atlanticwood® pine boards have several applications, but are mainly used for exterior decking and the cladding facades of buildings. The LCA study was conducted based on the ISO 14040/44 standard and PCR "Product Category Rules for preparing an environmental product declaration for Construction Products and Construction Services". Because the precise function of the product or scenarios at the building level is unknown the declared unit is used instead of the functional unit. The declared unit is applicable for an EPD that covers "cradle to gate" and in this case is 1 m^3 of Atlanticwood® pine boards. The inventory datasets for the products and processes included in the system boundaries were obtained from the company (specific data). Generic data were obtained and adapted as necessary from the Ecoinvent 3.1 database and from Franklin USA. The inventory analysis and, subsequently, the impact analysis was carried out using the SimaPro8.0.4 LCA software and associated databases and methods. The method chosen for the impact assessment was EPD (2013) V1.01. The results show that more than ¾ of "Acidification", "Eutrophication", "Global warming" and "Abiotic depletion" caused by 1 m^3 of Atlanticwood® pine boards production is due to energy consumption (electricity + gas + biomass). This was to be expected since the treatment is based on the production of heat and no chemicals are added during the heat treatment process.

INTRODUCTION

The environmental performance of products is a growing concern for most companies due to increasingly restrictive legislation and the greater awareness of consumers about environmental issues. Santos & Santos Madeiras (S&S) is a Portuguese company, certified by the FSC® (Forest Stewardship Council®), which has all its activity in the forestry sector, mainly in wood products processing. S&S decided to undertake Life Cycle Assessment (LCA) studies on their products in order to later carry out an Environmental Product Declaration (EPD).

Atlanticwood® is the registered trademark of the S&S thermally modified wood products manufactured using the Thermowood® method (ThermoWood 2003). Thermal treatment is a technologically advanced process involving the use of three variables only: heat, pressure and moisture. Wood is gradually heated to temperatures ranging from 160ºC to 230ºC, which changes its molecular structure making it more dimensionally stable and resistant to biodegradation and imbuing it with properties similar to those of tropical species. The thermal treatment turns the color of the wood darker and gives it a warmer hue. The process for the production of thermally modified wood uses no chemical compounds at all, thereby avoiding harmful effects to the environment and no substances whatsoever are added during the treatment. The total absence of chemical compounds preserves the natural beauty of the wood, ensuring it blends in perfectly with numerous decorative solutions and maintains an all-round uniform colour.

The thermal treatment used in S&S varies from medium to high intensity. Thermo I – intense treatment – is conducted at a higher temperature level. The resulting products feature a high degree of dimensional stability and durability, significantly increasing the service life of the item. The intensive treatment of the wood ensures that it can be used both indoors and outdoors. It is most commonly used for lining walls and cladding (indoors and outdoors), indoor floors and decking. Thermo S – soft treatment – is a medium-temperature treatment that increases the stability of the wood, giving it a bright shiny to a medium brown (honey) tone. The soft treatment is recommended for indoor use exclusively, such as in flooring, linings and other decor.

LCA is a technique for assessing the environmental aspects and potential impacts associated with a product (ISO 14040; ISO 2006a, ISO 14044; ISO 2006b) and has been used by industry in many situations (European Platform on LCA), for example to help reduce overall environmental burdens across the whole life cycle of goods and services, to improve the competitiveness of a company's products or to communicate with governmental bodies. It can also be used in decision making, as a tool to improve product design (for example the choice of materials), the selection of technologies, specific design criteria and when considering recycling, or in benchmarking of product system options, in purchasing decision making and technology investments, innovation systems, etc. The benefit of LCA is that it provides a single tool that is able to provide insights into the upstream and downstream trade-offs associated with environmental pressures, human health and the consumption of resources.

EPDs or Environmental Product Declaration Type III (ISO 14025; ISO 2006c) is a set of quantified environmental data consisting of pre-set categories of parameters based on Life Cycle Assessment according to the ISO 14040 series of standards, with at least a minimum set of parameters for each product group (Bogeskär *et al*. 2002). EPDs have to meet and comply with specific and strict methodological prerequisites to the product group, so-called, Product Category Rules (PCR). Product Category Rules for preparing an environmental product declaration for Construction Products and Construction Services are published by International EPD® System (PCR, 2014).

The aim of the present work was to conduct a LCA (cradle to gate) study of Atlanticwood® pine boards (Thermo I) based on real data provided by S&S to help the company management reduce overall environmental burdens across the life cycle of the product.

EXPERIMENTAL

The LCA (cradle to gate) study of Atlanticwood® pine boards was performed on the basis of the ISO 14040/44 (2006) standard and PCR 2012:01 recommendations (PCR, 2014).

According to ISO 14040/44, the LCA is divided into four phases: 1) goal definition – which defines the aim and scope of the study as well as the functional unit (a measure of the function of the system studied); 2) inventory analysis – which lists emissions of pollutants into air, water and soil, solid wastes and the consumption of resources per functional unit; 3) impact assessment – which assesses the environmental impact of the pollutants emitted throughout the life cycle; and 4) interpretation of results.

According to PCR 2012:01 the environmental impact per declared unit for the following environmental impact categories shall be reported in the EPD, divided into core, upstream and downstream module and the stages A to C and D if relevant according to EN 15804 (2012): global warming, kg CO_2 equivalents (GWP100); biogenic carbon stored in products, kg CO_2 equivalents (optional); ozone depletion, kg CFC 11 equivalents; acidification of land and water, SO_2 equivalents; eutrophication, PO_4 - equivalents; photochemical ozone creation, C_2H_2 equivalents; depletion of abiotic resources (elements), kg Sb equivalents; depletion of abiotic resources (fossil), MJ net calorific value. In Europe, the characterization factors outlined in EN 15804 (CML baseline) shall be used.

Goal and scope of the study

Goal of the study

The main aim of this study was to conduct a LCA (cradle to gate) to assess the potential life cycle environmental impacts associated with Atlanticwood® pine boards (Thermo I) produced by the S&S company. The results of the study were to be communicated to the company decision makers who could assess the environmental profile of the products and indicate areas where opportunities exist to improve its overall environmental impacts. Another aim of this study was to prepare an environmental product declaration for Atlanticwood® pine boards.

Scope of the study

The study was based on Atlanticwood® pine boards (Thermo I) with a length of 0.6 - 2.6 m, width of 100 – 120 mm and thickness of 26 mm, to reach a durability level which complies with the requirements for durability class 3.2 according the EN335-2 (2006) standard and to be used in the construction of exterior decks or cladding.

Functional unit

The declared unit is used instead of the functional unit, because the precise function of the product or scenarios at the building level are unknown. The declared unit is applicable for an EPD that covers "cradle to gate" and in this case is 1 m^3 of Atlanticwood® pine boards.

System boundary

The system boundary for the product system is represented in a simplified way in Fig.1.

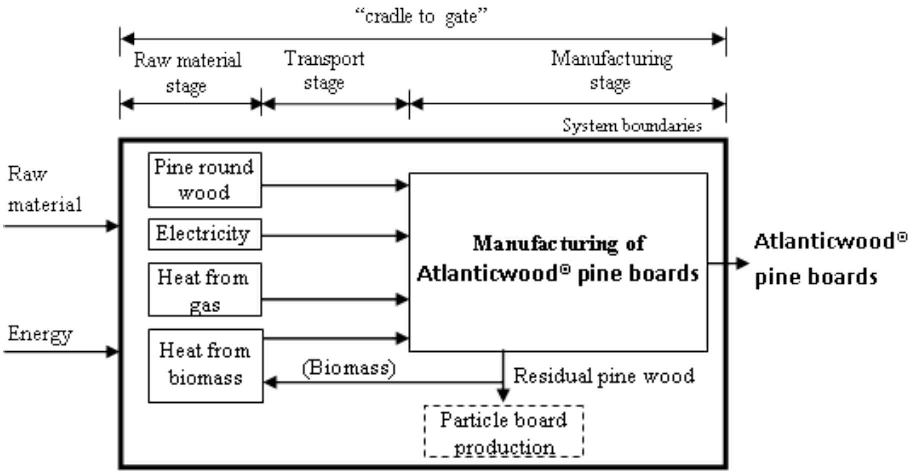

Figure 1: The system boundaries of the study

The product system delivers a secondary raw material (residual pine wood) that can be used as raw material for another product system (particleboard production). To solve this allocation problem the system boundaries were expanded to include particleboard production.

EPDs, “cradle to gate”, correspond with the product stage and the modules to be included in the boundaries are the information modules A1-A3: A1- raw material extraction and processing, processing of secondary material input (e.g. recycling processes); A2- transport to the manufacturer; A3- manufacturing.

Inventory analysis

The inventory analysis and, subsequently, the impact analysis have been performed using the LCA software SimaPro 8.0.4 (PRé Consultants) and associated databases and methods.

Data type/data collection

The inventory datasets for the products and processes included in the system boundaries are presented in Table 1. They are the company's data and relate to the year 2014. Almost 100% of the wood comes from forests in the region where the S&S facilities are located. All the materials and energy used for the production of 1 m^3 of Atlanticwood® pine boards were accounted for, excluding packaging.

Table 1: Inventory datasets for 1 m^3 of Atlanticwood® pine boards manufacturing

Inputs		**Outputs**	
Pine round wood	4.587 m^3	Atlanticwood® pine boards	**1** m^3
Electricity	267.294 kWh	Residual pine wood for particle board production (out)	2.727 m^3
Heat from Gas (propane)	42.133 kg (542.392 kWh)	Residual pine wood for inside heat production (biomass)	0.860 m^3
Heat from biomass (residual pine wood)	0.860 m^3 (2024.482 kWh)	Water	0.229 m^3
Transport of pine round wood	156 t.km		
Water	0. 229 m^3		

The following assumptions were made for the inventory datasets:

- The pine round wood (4.587 m^3) with a moisture content of (u=70 %) and density of (d=680 kg/m^3) is transported from the forest to the company an average distance of 50 km.
- As the product system delivers a quantity of residual pine wood (2.727 m^3) for particle board production impacts from the same quantity of industrial wood production (at forest road) was considered to be avoided.
- The infrastructure for the production facilities of the thermally-modified pine board was not taken into account as it has been assumed that its contribution to the overall impact is negligible (Jungmeier et al. 2002).

The inventory datasets for the background system (such as electricity) were obtained and adapted as necessary from databases presented in SimaPro 8.0.4 software and other sources as recorded in Table 2.

Table 2: Inventory data for the background system

Process	Equivalent process	Source
Pine round wood	Round wood, softwood, under bark, u=70% at forest road/PT U	Ferreira and Domingos (2012)
Electricity	Electricity, low voltage, at grid/PT U	SimaPro 8.0.4 - Ecoinvent database (adapted according to electricity source of EDP 2014)
Heat from gas (propane)	Heat from LPG FAL	SimaPro 8.0.4 - Franklin USA 98 database
Heat from biomass (residual pine wood)	Wood chips, from industry, softwood, burned in furnace 1000kW/CH U-adapted	SimaPro 8.0.4 - Ecoinvent database
Residual pine wood for particle board (production out)	Industrial wood, softwood, under bark, u=102%, at forest road/PT U	Ferreira and Domingos (2012)
Transport of pine round wood	Transport, freight, lorry >32 metric ton, EURO5 {GLO}|market for| Conseq, U	SimaPro 8.0.4 - Ecoinvent database

Life cycle impact assessment (LCIA)

The method chosen for impact assessment was EPD (2013) V1.01 (SEMC, 2013) ready to use in SimaPro software. All impact categories are taken directly from CML-IA baseline method (eutrophication, global warming, photochemical oxidation, ozone layer depletion and abiotic depletion) and CML-IA non baseline method (acidification).

RESULTS AND INTERPRETATION

The following (Table 3 and Figure 2) show the unit process contributions from the production of 1 m^3 of Atlanticwood® pine boards (Thermo I) on the impact categories considered.

Table 3: Impact assessment (characterization)

Impact category	Unit	Total	Electricity	Heat from gas	Heat from biomass	Transport of pine round wood	Pine round wood	Residual pine wood for particle board
Acidification (fate not incl.)	kg SO2 eq	1.728	0.871	0.156	0.544	0.051	0.406	-0.300
Eutrophication	kg PO4--- eq	0.472	0.269	0.029	0.137	0.031	0.083	-0.077
Global warming (GWP100a)	kg CO2 eq	279.502	117.454	134.437	6.529	12.394	48.875	-40.187
Photochemical oxidation	kg C2H4 eq	0.124	0.032	0.009	0.014	0.002	0.124	-0.056
Ozone layer depletion (ODP) (optional)	kg CFC-11 eq	1.12E-05	4.86E-06	7.70E-08	8.7E-08	2.56E-06	8.7E-06	-5.19E-06
Abiotic depletion (optional)	kg Sb eq	1.36E-04	2.52E-04	4.06E-09	8.7E-06	9.73E-06	1.9E-05	-1.54E-04

Sending the pine wood residues resulting from the Atlanticwood® pine board production process the manufacture of "particleboard" allows a reduction (negative sign in Table 3 and Figure 2) in all categories of impact, with a 53% reduction in "Abiotic depletion", 31% in "Photochemical oxidation" and 32% in the "Ozone layer depletion (ODP)". The reduction in other indicators, although below the former, are still significant, representing 15% on acidification, 14% on eutrophication and 13% on global warming. It should be noted that the contribution of pine round wood transport is almost insignificant to all the environmental indicators (1%-6%) except for the ozone layer depletion (ODP) that contributes 16%.

Acidification

The main source of this indicator is electricity consumption at approximately 43%. Another 27% applies to heat from biomass and 20% to pine round wood at the forest road. Heat from gas only accounts for 8%.

Eutrophication

The eutrophication is similar to the acidification in terms of its distribution.

Global warming (GWP100a)

Approximately 42% of the indicator value applies to heat from gas, 37% to electricity consumption and 15% to pine round wood at the forest road. The indicator for the transport of pine round wood is a mere 2%.

Photochemical oxidation

The main source of this indicator is pine round wood at the forest road with 69%. Another 18% applies to electricity consumption. Heat from biomass only accounts for 8% and heat from gas 5%.

Ozone layer depletion (ODP)

54% of the indicator value applies to pine round wood at the forest road, 30% to electricity consumption and 16% to the transport of pine round wood. Heat from biomass only accounts for 1%.

Abiotic depletion

Electricity consumption is the main source of this indicator at 87%. Pine round wood at the forest road is responsible for 7% of this indicator. Transport of pine round wood and heat from biomass each contribute 3%.

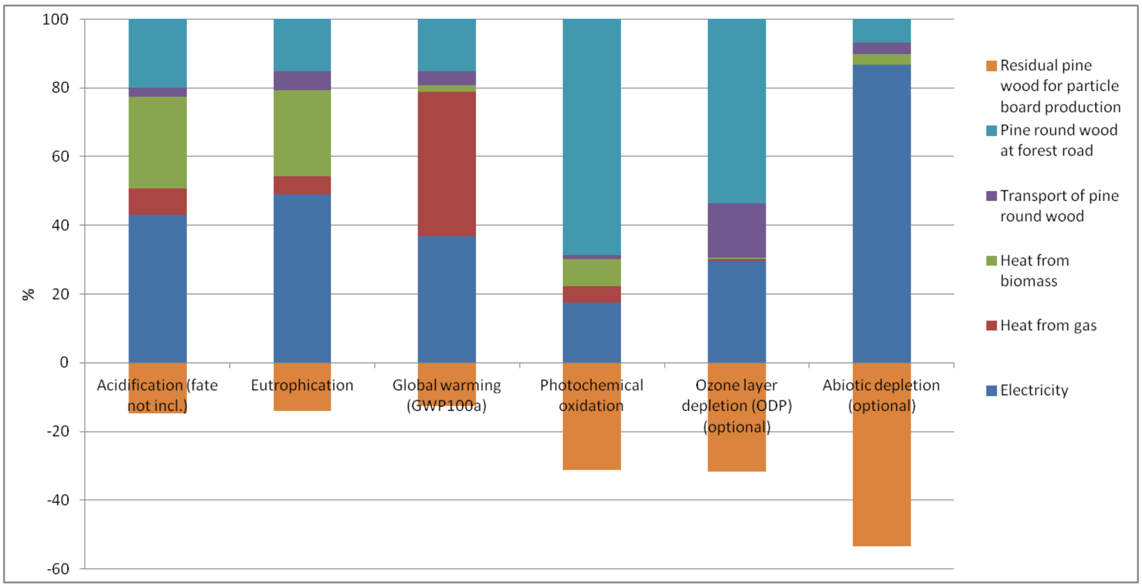

Figure 2: Environmental profile of 1 m^3 Atlanticwood® pine boards. Method: EPD (2013) V1.01 / Characterization

CONCLUSIONS

The results show that more than ¾ of “Acidification”, “Eutrophication”, “Global warming” and “Abiotic depletion” caused by 1 m^3 of Atlanticwood® pine boards production is due to energy consumption (electricity + gas + biomass). Pine round wood production is the process that contributes most to the other impact categories “Photochemical oxidation” and “Ozone layer depletion (ODP)”.
This was to be expected since the treatment is based on heat production and no chemical are added during the heat treatment process. The amount of energy necessary for the treatment is much higher than used in wood processing activities.

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Study on the Microstructural Changes of Thermo-Hydro Treated Wood Using X-ray Computed Tomography

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ABSTRACT

In this paper X-ray computed tomography (µCT) was used in order to investigate and visualize the anatomical structural changes in a selection of soft- and hardwoods after thermo-hydro-treatment (THT). A specific sequence of sample preparation, X-ray scanning and volumetric processing was developed within the frame of this investigation. Needle-shape specimens of soft and hardwoods wood were scanned using the state-of-the-art micro CT scanner at the Gent University Center for X-ray Tomography (UGCT). An approximate voxel pitch between 0.8 and 1.2µm^3 was applied to investigate the changes in relevant microscopic features of wood induced by THT. The same wood volumes were examined before and after treatment at 160°C and quantitative data of individual parameters (maximum opening and lumen volume) for various cell types were obtained by using Morpho+, tailor made processing software. It is essential to map these changes before and after treatment to assess the level of changes to come to a proper dose-response interpretation of the treatment, as well as a quality indicator for established treatments themselves. The highest values of substance volume were recorded for ash latewood (81%) and pine specimens (72%). A significant correlation between the wood substance gravimetrical mass loss and X-ray volume loss after THT was found. When evaluating individual fiber parameters, the largest difference was found in the lumen volume of several tissue component types (libriform, tracheid and ray parenchyma) between wood species. The average aspen fiber volume reduction after THT was 31%, a value 2.6 times higher than the volume reduction of the average vessel. These results prove that changes in the relevant microscopic features of wood can be induced differently. Thus, the microstructural changes of THT wood can be investigated by quantifying changes in wood volume, porosity and individual parameters using X-ray CT scanning.

INTRODUCTION

In the last decade several new thermal modification (TM) processes were developed by Wood Treatment Technology (WTT) in Denmark, Vacuu^3 (Opel-Thermo) in Germany and Firmolin® in the Netherlands. The main difference between a one-stage THT process and a multi-stage process, is that the different steps (hydrothermolysis, drying, and partial curing) have been combined, so that the treatment can be carried out within a single piece of equipment (autoclave).

During THT wood passes through the three treatment stages (see below – *EXPERIMENTS*), where the main processes which occur in each stage are completely different and the wood tissue during the treatment swells and shrinks. In the first stage, several simultaneous processes take place, but the most dominant are mass and heat transfer processes like absorption and heating. Heating and swelling of wood cell walls occur. In the second stage, apart from mass and heat transfer processes, the most dominant are chemical reactions. A chemical transformation of the cell wall components through autocatalytic reactions induced by heat in a saturated steam medium take place. In the third stage diffusion and evaporation of low molecular weight compounds from the wood cell walls and shrinking happens. These irreversible transformations alter the wood microstructure, and the extent of the modifications is dependent on the initial chemical composition and microstructure of the wood, the treatment atmosphere (saturated or superheated steam, nitrogen, air or hot oil) and process parameters (temperature, duration, pressure) (Zaman *et al*. 2000).

Therefore, it is essential to map these changes before and after treatment to assess the level of change, to come to a proper dose-response interpretation of the treatment, as well as a quality indicator for established treatments themselves. Many techniques are available to investigate these properties, ranging from very simple methods for point measurements to in-depth three-dimensional characterization. Clearly, most of these are either limited to surface or sub-surface examination and/or are destructive in nature.

TM wood has been the subject of different microstructure investigations in previous studies by Fengel (1966), Filló and Peres (1970), Gosselink *et al*. (2004), Boonstra *et al*. (2006), Awoyemi and Jones (2010). In these studies the microstructure of wood and the effect of the heat treatment process on the individual fibers are usually studied by scanning electron or light microscopy. However most of the work published before provides only limited information about the entire 3D structure of thermo-hydro treated wood. Therefore, a powerful addition to existing methods is X-ray tomography.

X-ray computed tomography and accompanying image analysis have been successfully used in some of investigations concerning wood microstructure characterization. The number of papers with focus on lab-based X-ray tomography for fundamental research as well as its use as a tool for structural analysis is steadily increasing. Van den Bulcke *et al*. (2009, 2013) illustrated the power of X-ray computed tomography as a tool for both descriptive and quantitative identification of wood anatomy to resolve details on three-dimensional reconstructions at near sub-micron scale and its use for wood modification in general. Being non-destructive in nature, X-ray CT avoids potential artifacts introduced by sample preparation, which is a key advantage that allows monitoring and quantification of the effect of wood treatment on the same specimen.

In this study, scans on needle shaped specimens of a selection of soft- and hardwoods were performed using the X-ray µCT Nanowood scanner of the UGCT, with focus on visualization and the quantification of 3D microstructural changes due to THT. The aim of this study was to assess the general microstructural changes in soft- and hardwood tissue elements as a result of THT.

EXPERIMENTS

The following woods were in focus: birch (*Betula pendula*), aspen (*Populus tremula*), grey alder (*Alnus incana*), ash (*Fraxinus excelsior*) earlywood (EW) and latewood (LW), spruce (*Picea abies*) and Scots pine (*Pinus sylvestris*). The samples were prepared from larger blocks and subdivided with a scalpel into needle-shaped specimens measuring approximately 0.4 x 0.4 x 6 mm^3. The specimens were oven-dried and stored in a desiccator. The same specimens were scanned before and after THT at 160°C.

THT was carried out in a pilot-scale 560 l stainless steel autoclave produced by WTT. The reactor temperature was maintained by circulating hot mineral oil in the jacket. The working THT cycle diagram at 160°C comprises three steps: (I) heating, (II) 1-h incubation at 160°C, and (III) a final cooling. A known quantity of water, which depended on the initial amount of water in the wood and the batch volume, was pumped in at the beginning of the process to improve the heat transfer from the autoclave walls and to increase the reactivity of the cell wall components at relatively low temperature. The rate of the process parameters was increased or decreased during the heating and cooling steps to avoid artificial crack formation.

The mass loss (ML) of the THT specimens was calculated as

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

where ML is the ML due to THT, m_0 and m_1 are the oven-dried masses of the specimens before and after THT, respectively. Four replicates per species were considered for the calculation of the average ML.

Oven-dried untreated and THT-treated specimens were subjected to identical acquisition and analysis procedures.

Image acquisition: All specimens were mounted on a holder, and the central region of all wood samples (approximately 1 mm in height depending on the resolution) was scanned by the Nanowood scanner at the Center for X-ray Tomography at Ghent University (UGCT, http://www.ugct.ugent.be) as described by Dierick *et al*. (2014). The coordinates of the central region were recorded before treatment to enable the same region to be scanned after treatment. This flexible, state-of-the-art scanner is controlled by in-house developed software with a generic interface (Dierick *et al*. 2010). All wood pieces were scanned at an average voltage of 55 kV, a target current of 160 µA, and an exposure time of 1500 ms per image, resulting in an approximate scan time of 45–60 min per object. Reconstruction was performed with Octopus (Vlassenbroeck *et al*. 2007), which is a tomography reconstruction package for parallel and cone-beam geometry, with ca. 20 min per scan. All specimens were filtered by the phase contrast method in Octopus (De Witte *et al*. 2009; Boone *et al*. 2009). The resulting high-resolution scans had an approximate voxel pitch of 0.8–1.2 μm^3 with 2^{16} grayscale levels. Reconstructed images of the samples before and after THT were visualized by Octopus Analysis (www.insidematters.be, previously known as Morpho+, Brabant *et al*. 2011) and rendered into 3D images by means of VGStudio MAX.

Image preprocessing: Preprocessing was performed in Morpho+. For correct analysis, rotation of the volume was necessary such that the three major wood axes (x = tangential, y = radial, z = axial) were aligned properly according to the virtual cross-sectional planes. Bilateral filtering with edge preservation to reduced noise was used (Tomasi and Manduchi 1998). The volumes were then binarized, and the volume of interest (VOI) was determined, ensuring the same VOI for both THT and reference samples. Subsequently, the volume was thresholded once more within the VOI to differentiate air and wood, which enabled calculation of the porosity and the volume of wood tissue to be undertaken. Cell wall porosity is not considered here due to the inherent resolution limitation of X-ray CT and the partial volume effect; therefore, only larger pores with volumes around 1 μm^3 or larger were detected.

Image segmentation and calculations: Filtered volumes with binarized cell lumens were labeled, distance transformed, and separated via the watershed operation, resulting in segmented lumens of different cell types and vessels. The effects of THT on hardwood (HW) and softwood (SW) were evaluated according to the "good fibers/good vessels" principle. A fiber or vessel lumen is considered good when clearly separated and not connected with the lumens of other fibers or vessels. Split lumens, due to over-segmentation, were rejoined manually. Through careful visual selection, it was possible to locate the same cells (vessels, libriform fibers, tracheids…) in both the untreated and treated specimens. The volumetric changes of the specimens were calculated based on the 3D data.

The total amount of wood tissue (WT) voxels in the VOI (V_{WT}) was calculated according to

$$V_{WT} = (V_{VOI} - V_L) \times v_p \qquad (2)$$

where V_{VOI} represents the total number of voxels in the VOI, V_L represents the total number of lumen voxels (voids) in the VOI, and v_p represents the approximate voxel pitch.

The porosity within the VOI was calculated according to

$$Porosity\ (\%) = 100(V_L/V_{VOI}) \qquad (3)$$

The maximum opening was calculated automatically by Morpho+ and was based on a virtual sphere with a maximum diameter that could fit inside the fiber lumen without having any common point (voxel) of contact with the cell wall material (voxel); hence, the maximum opening is the maximum-inscribed sphere in the cell lumen.

More detailed description of experiment you can find under Biziks *et al.* (2015).

RESULTS

Microstructural changes induced by THT

The specimens were subjected to thermo-hydro treatment (THT) in a saturated steam atmosphere in a pilot-scale autoclave at 160°C for 1h. During the treatment the autohydrolysis (dehydratation) of the hemicelluloses and the evaporation of low molecular weight compounds (acetic and formic acid, furanaldehyde, water) occurs and are thus removed from the matrix, resulting in mass loss, shrinkage and hence changes to the microstructure. The changes recorded after the treatment of needle-shaped specimens could be comparable with what happens at the surface of larger objects.

The mass loss (ML), porosity and total volume change of the specimens and cell wall material in the specimens are given in Table 1 for the THT wood of the different species.

Table 1: Data concerning the (VOI) as derived from thermo-hydro treated wood (THT) by X-ray tomography scans

Species	ML* [%]	Total volume loss		Porosity [%]	
		CW** [%]	Volume [%]	Before THT	After THT
Gray alder	16	-19	-17	42	46
Aspen	21	-16	-18	37	32
Birch	16	-17	-19	34	29
Ash eW[a]	24	-19	-9	41	56
Ash lW[b]	15	-17	-16	19	16
Pine	15	-17	-17	28	28
Spruce	16	-8	-3	48	54

*Mass loss is measured gravimetrically; **Cell wall material [a] – earlywood (eW), [b] – latewood (lW)

Slight differences in ML were apparent between the different wood species for softwood (15-19%) and for hardwood (17–24%), respectively. As mentioned before, the amount of wood voxels in the specimens before and after treatment could be related to the weight loss. As shown in Table 1, the total volume loss of cell wall material and ML between different wood species, except for spruce, did not differ much and shows the feasibility of using the wood voxels as an indicator of the amount of wood lost during treatment. Possible differences in the results between ML and loss of wood voxels can probably be attributed to an increase or reduction in cell wall material during thresholding and the fact that only a very small part of the sample is scanned and the entire sample is weighed. It is possible that certain regions in the entire needle shaped specimens have larger shrinkage and ML than in the VOI. The higher ML of hardwoods can be attributed to higher amount of hemicelluloses compare to softwoods, which are the constituents of wood with the highest susceptibility to thermal decomposition Bourgois *et al.* (1989).

Visualizing the exact same region of the specimen before and after THT clearly illustrates shrinkage (Figure 1). For proper understanding, the dimensions of the samples were not physically altered. The top of the grey (= untreated) volumes were virtually cut to show the brown (= treated) sample clearly. Larger shrinkage was observed in the tangential direction than in the radial direction. Generally all wood specimens had a similar reduction in volume of about 17% (Table 1), whereas for ash EW and spruce the shrinkage was respectively 2 and 6 times smaller, compared to the other wood species. One explanation could relate to the total amount of wood or wood cell wall thickness. During the cooling stage, diffusion and evaporation of low-molecular-weight compounds occurs. Simultaneously, the free space between the macromolecular constituents gradually decreases, and a rearrangement of the matrix can take place. A reduction in size in the single cell could be explained by the fact that the macro-molecules still interact through different types of bonds. Probably they have the tendency to occupy a more energy-efficient layout, and due to plasticity, they try to pull each other. The distances between the macromolecules decrease and result in shrinkage of the single cell. Displacement, which equals shrinkage in this case, of a cell, could occur through the middle-lamella, which binds cells together. The amount of distribution of constituents in the thin cell wall could be much lower and could result in minor shrinkage of the sample. A different reduction in the size of the cell wall as a result of THT was observed previously Biziks *et al.* (2013). This study considered that the treatment impact is different for different types of cells.

The porosity of a specimen can be constant before and after the treatment only if the change in volume of the wood cell wall equals the change of the total volume of the VOI; this was observed for pine and ash LW. The data in Table 1 gives evidence that for all other species the cell wall and total volume changes were different. A good correlation between wood substance and shrinkage (total volume changes) was found. Species with less cell wall material, in this case alder, ash EW and spruce, have a higher porosity after THT compared to wood species like birch and aspen. The former shrunk less than the latter, but at the same time have nearly the same weight loss of wood.

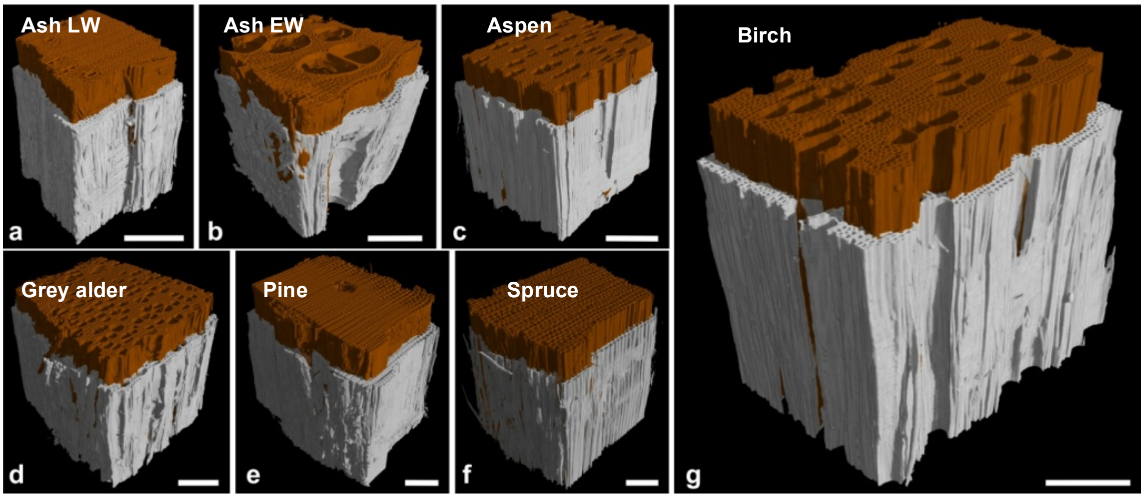

Figure 1: 3D renderings of X-ray tomography volumes: ash LW (a), ash EW (b), aspen (c), gray alder (d), pine (e), spruce (f) and birch (g). Untreated samples are grey, and treated specimens are dark brown. Scale bar: 200 µm.

A full description of the results can be found in Biziks *et al.* (2015).

CONCLUSIONS

X-ray micro-CT was found to be an adequate method for 3D characterization of the microstructural changes occurring in wood as a result of THT and it allows visualization and quantification of the shrinkage caused by the process. Analysis of the X-ray data of the initial specimen's volume showed that the volume occupied by the cell wall material obviously differs from one wood species to another.

The volume and maximum opening of the fiber lumen differ from one wood species to other, but in generally the reduction in volume was 2 to 4 times higher than for vessels.

The porosity of the specimens after THT was also investigated, and was found to vary significantly between different species, which indicated that different levels of interaction between the different types of tissue takes place. Porosity data show that the same rate of process parameters cannot be applied to all wood species. In lower density wood specimens (like alder or ash EW) the same heating and cooling rate resulted in porosity increases that impair the final product properties (mechanical strength, water absorption rate and penetration depth).

X-ray CT and the image processing protocol as presented in this paper for the study of THT of wood, can be used for many other purposes in which the evaluation of a certain treatment is of importance, e.g., the dynamic processes what occur in wood can be evaluated by X-ray CT, for example the rate of cell wall penetration (bulking).

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Pretreatment of Veneers with Hydrogen Peroxide for Self-Bonded Laminated Boards

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Keywords: beech, ferrous sulphate, oxidant, swelling, shear strength, oxidant, veneer

ABSTRACT

Self-bonded veneers could be an environmentally friendly alternative to the use of synthetic adhesives in the making of laminated boards. This paper describes the influence of an oxidative treatment of beech veneers using hydrogen peroxide and an iron catalyst on the properties of 2-ply laminated veneer boards formed by hot-pressing at 230-250°C. The mass loss of boards made from veneers that had undergone oxidative treatment rose with increasing press temperature and the mass loss was higher for boards made from treated veneers than without treatment. Boards from oxidative treated veneer pressed at 230°C had higher shear strength than untreated ones both before and after wet cycling. Swelling in water decreased with increasing press temperature and the results indicate that swelling of the boards in water was less when oxidatively activated veneers were used instead of untreated veneers.

INTRODUCTION

The use of adhesives is still an issue within the board industry as end-user demands on environmentally safe boards are high. A method has been developed to produce self-bonded laminated boards from veneers without the use of synthetic adhesives (Cristescu 2006, 2008, Cristescu *et al*. 2015) and it was found that properties such as the shear strength and the swelling of boards were strongly related to press conditions such as temperature and pressure and the duration of the pressing time applied. Furthermore, a method for producing particleboards and fiberboards without using synthetic binders such as urea-formaldehyde has been presented (Westermark and Karlsson 2002, Karlsson *et al*. 2006), involving the pretreatment of the wood particles or fibers with hydrogen peroxide and a ferrous sulfate catalyst under relatively dry conditions followed by hot pressing at temperatures of 170-200°C. The pretreatment gave boards with high resistance to swelling in water, and this encouraged us to study the influence of such an oxidative treatment on veneers for self-bonded laminated boards.

EXPERIMENTAL

Rotary-cut veneers (100x70x2.1 mm^3) from beech (*Fagus sylvatica* L.) with a dry density of ca. 625 kg/m^3 were treated by spraying an aqueous solution of ferrous sulphate $FeSO_4x7H_2O$ (0.1% odw) followed by 0.5% hydrogen peroxide on one side of the veneer. The veneers (MC 8.5%) were then pressed into laminated veneer boards with their treated sides against each other in a laboratory press at 230, 240 and 250°C under a pressure of 5.2 MPa for 240 s. During each pressing operation, two boards from veneers treated with hydrogen peroxide and two boards from veneers treated without hydrogen peroxide were performed. At a pressing pressure lower than 5.2 MPa some delamination occurred when the board was soaked in water and conditioned at 23°C and 50% R_H and boards pressed at a lower pressure were therefore not included in the study. Four boards from each variation (pressing temperatures: 230, 240, 250°C, and from veneers treated with or without hydrogen peroxide), making a total of 24 boards, were prepared. Boards conditioned at 23°C and 50% R_H, in a climate chamber were cut along the grain for shear strength testing according to SS-ISO 6237:2004 resulting in 48 samples. Half of the boards were kept at 23°C and 50% R_H while the other half of boards were subjected to a cycle comprising soaking in water for 24 h, conditioning, then soaking in water and finally conditioning at 23°C and 50% R_H.

The thicknesses of the conditioned veneers and the corresponding boards were measured and the percentage thickness reduction (TR) was calculated. The percentage thickness swelling (TS) of the conditioned boards soaked in water for 24 h as well as the corresponding water absorption (WA) as a percentage of conditioned mass were determined. The percentage mass loss during formation of the boards was calculated based on the calculated dry weight of the veneers before activation and of the corresponding boards after hot-pressing. The equilibrium moisture content (EMC) of boards at 23°C and 50% R_H and 23°C and the percentage thickness shrinkage (TSH) of the conditioned boards were determined by drying the boards over-night at 103°C.

RESULTS AND DISCUSSION

Laminated boards were produced from veneers pretreated with and without hydrogen peroxide and an iron catalyst by pressing pairs of veneers together along the grain (parallel orientation of the veneers) at 230°C to 250°C. Figure 1 shows boards after shear strength testing.

Figure 1: Samples of boards pressed at 230, 240 and 250°C after shear testing. Boards from veneers treated (left) without and (right) with hydrogen peroxide

The veneers turned a brownish colour when pressed into boards, and the boards became somewhat darker with increasing press temperature (Fig. 1). The bond-line of the samples became visible as the darker parts after the shear-strength test and it could be seen that the bond-lines were darker in boards that were made from pretreated veneers than in those that were not pretreated (Fig.1). The shear strength of boards pressed at 230°C was higher in boards made from treated veneers than in boards made from untreated veneers (Fig. 2).

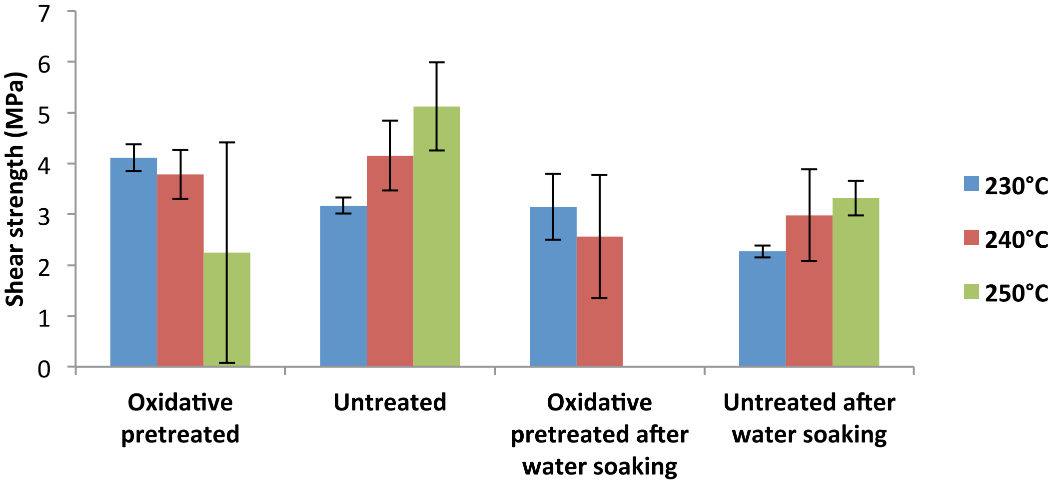

Figure 2: Shear strength of boards pressed at 230, 240 and 250°C

The shear strength of boards pressed at 240°C from untreated veneers was similar to that of boards from treated veneers pressed at 230°C. Wet cycled boards (see below) were weaker, but boards from treated veneers seemed to be stronger than boards from untreated veneers when pressed at 230°C. At 250°C the presence of blowholes as well as tensile rupture obscured the results for the boards made from treated veneers. A decrease in tensile strength for veneers treated with Fenton's reagent (hydrogen peroxide and ferrous sulphate) has been reported (Xie *et al.* 2010).

The reduction in the thickness of the conditioned boards rose with increasing press temperature (Table 1). Both boards made from pretreated veneers as well as from untreated ones could withstand swelling in water over night and conditioning for two cycles without any sign of delamination.

Table 1: Properties of boards from veneers treated with or without hydrogen peroxide and ferrous catalyst: Thickness reduction after pressing (TR), Thickness swelling in water after 2nd cycle (TS), Water absorption after 2nd cycle (WA). Standard deviation within parenthesis

Press temperature [°C]	TR [%]	TS [%]	WA [%]
230[a]	31.7 (5.2)	30.9 (2.1)	71.2 (1.0)
230[b]	36.0 (0.5)	25,6 (0.6)	50.9 (4.2)
240[a]	39.2 (7.3)	21.5 (1.8)	54.1 (9.3)
240[b]	39.2 (2.3)	18.7 (0.7)	39,4 (1.3)
250[a]	44.5 (4.7)	17.3 (0.7)	38.8 (1.9)
250[b]	44.4 (4.4)	18.5 (2.6)	37.0 (3.9)

[a]*Boards from veneers treated with neither hydrogen peroxide nor a ferrous catalyst,* [b]*Boards from veneers treated with hydrogen peroxide and ferrous catalyst*

Of the boards pressed at 230°C and 240°C, those made from untreated veneers swelled somewhat more in water than those made from pretreated veneers (Table 1). The thickness swelling in water of boards from wood fibers as well as wood particles has been found to be reduced by a similar oxidative pretreatment (Westermark and Karlsson 2002, Widsten 2002). The water absorption (WA) on soaking followed a trend similar to that observed for the swelling (Table 1).

The mass loss for boards from veneers treated with hydrogen peroxide and ferrous catalyst increased with higher press temperature (Fig. 3). The results showed that the mass loss for the boards made from treated veneers was higher than for boards prepared without the oxidative pretreatment. The mass loss could be due to the degradation of wood components and the release of volatile substances, formed mainly during the hot pressing cycle, as well as to the evaporation of native extractives. Preliminary results indicated no great differences in the internal temperatures during pressing between boards made from treated and untreated veneers. The temperature of the veneers during pretreatment was close to ambient temperature. It cannot be ruled out that some volatile gases may be formed by reaction with wood during oxidative activation. Oxygen could also be formed by the iron-catalysed degradation of hydrogen peroxide, as small bubbles were observed on the wood surface after the chemicals had been sprayed onto the wood surface.

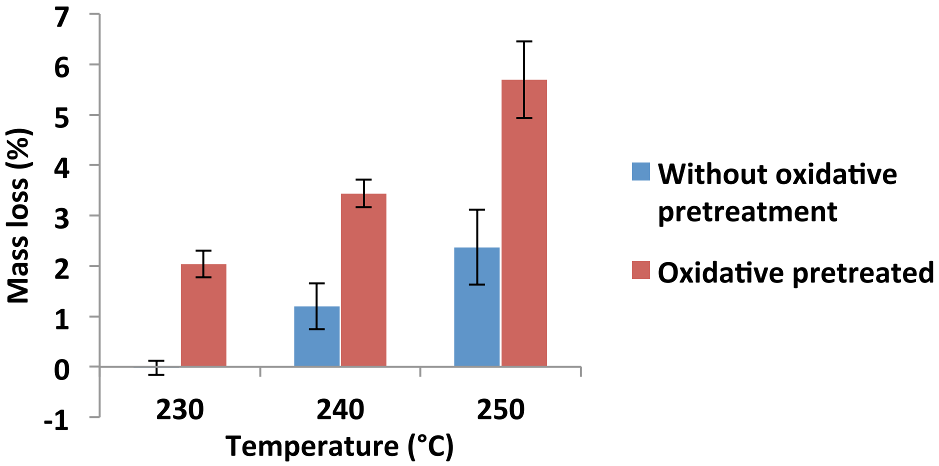

Figure 3: Mass loss during formation of board from oxidative pretreated veneers and veneers without pretreatment

It has been reported that acid groups are formed during such oxidative activation (Jenkin 1976). During the wet cycle test, water from the untreated boards was fairly neutral but it was slightly acidic (pH 4-5) from the pretreated boards. However, veneers treated only with ferrous catalyst resulted in boards that delaminated in water at room temperature. This indicates that it is the oxidation of the wood components rather than activation by the acidic ferrous catalyst that is important for achieving stable bonds between veneers during hot pressing.

The equilibrium moisture content (EMC) of the boards was reduced by increasing the press temperature (Table 2). The EMC of the conditioned boards increased after wet cycling and became close to the initial MC of the veneers (Table 2). An increase in the EMC of thermally modified wood has been observed after treatment under wet conditions (Obataya *et al.* 2000). A greater thickness shrinkage (TSH) was observed for wet cycled boards during the drying of conditioned boards than for ones only conditioned (Table 2). However, the boards were still stable and did not delaminate during the wet cycling test.

Table 2: Properties of boards from veneers treated with or without hydrogen peroxide and ferrous catalyst: Equilibrium moisture content (EMC) at 23°C, 50% R_H before and after 2nd water soaking, Thickness shrinkage (TSH) from EMC to dry material before and after 2nd water soaking

Press temperature	EMC [%]	EMC [%] after water soaking	TSH [%]	TSH [%] after water soaking
230[a]	6.5	11.2	4.6 (1.2)	7.8 (2.0)
230[b]	6.0	10.6	3.7 (1.3)	6.1 (1.3)
240[a]	5.8	10.6	3.5 (1.7)	4.9 (1.8)
240[b]	5.6	9.9	4.8 (1.8)	7.5 (1.4)
250[a]	4.9	9.8	4.4 (1.5)	7.6 (1.4)
250[b]	4.9	8.7	3.5 (1.0)	6.1 (0.6)

[a]Boards from veneers treated with neither hydrogen peroxide nor ferrous catalyst, [b]Boards from veneers treated with hydrogen peroxide and ferrous catalyst

CONCLUSIONS

From the results obtained so far, we suggest that it is possible to increase the stability and durability of self-bonded laminated veneer boards from beech by oxidative pre-treatment of the veneers using hydrogen peroxide and an iron catalyst before hot pressing.

Mass loss during formation of boards occurred. This, together with high temperature and high pressure, probably led to the formation of blow holes which were observed when pressing at the higher temperature especially in boards made from veneers that had undergone the oxidative pretreatment. Sufficiently mild conditions (a lower pressure for the same levels of temperature and time) should therefore be used during pressing to achieve boards with no blow holes.

In addition, preliminary results indicate that boards stable to boiling in water for 4 hours could be produced by hot pressing oxidative activated veneers under milder press conditions than the ones used in this study, whereas boards made from untreated veneers delaminated under those conditions. The preparation and selection of veneers could have an influence on the bonding and needs to be studied further.

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Improvement of a Method for Topochemical Investigations of Degraded Furfurylated Wood

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Keywords: brown rot degradation, furfuryl alcohol, lignin modification, modified wood, UV microspectrophotometry

ABSTRACT

The furfurylation of wood is a wood modification process where furfuryl alcohol molecules are allowed to penetrate into the wood cell wall and polymerizes *in situ*. This results in a permanent swelling of the wood cell wall (Stamm 1977). Brown rot basidiomycetes are the only known organisms capable of nearly completely removing polysaccharides from plant tissue, leaving lignin behind (Eriksson et al 1990). Lignin maintains its macromolecular nature throughout brown rot decay (Kirk 1975, Niemenmaa *et al.* 2008, Yelle *et al.* 2008), but their structure is modified substantially by hydroxyl radicals produced by the fungi (Yelle et al. 2008, 2011, Arantes *et al.* 2009, 2011, Martinez *et al.* 2011). UV microspectrophotometry (UMSP) is ideally suited to study the topochemical distribution of lignin in the wood cell wall (Fergus *et al.* 1969, Koch and Kleist 2001, Koch and Grünwald 2004). The UMSP technique enables direct imaging of lignin modification within individual cell wall layers. Rehbein and Koch (2011) detected topochemically the first signs of lignin modification by the brown rot fungus *Antrodia vailantii* in the S2 layer in *Pinus sylvestris* already after three days of incubation. We improved a method to investigate furfurylated *Pinus radiata* in order to gain a better understanding of the furfuryl alcohol polymerization process in the wood cell wall and to be able to detect early signs of brown rot degradation. The results from the method improvement indicate that cellular UV microspectrophotometry is a promising method to study early fungal degradation damages in the cell wall of furfurylated wood. Further degradation studies, where more data regarding decay will be collected, are planned to complement the results from this study.

INTRODUCTION

Wood applications in building and construction are faced with varying environmental conditions and a permanent presence of microbial organisms. Brown rot basidiomycetes are reckoned to cause the most destructive type of wood decay, even before any mass loss is detectable (Schultze-Dewitz 1966, Bariska *et al.* 1983, Winandy and Morrell 1993). Brown rot fungi attack the structural basis of the wood cell wall, cellulose and hemicelluloses, leaving a modified lignin behind (Danninger *et al*. 1980, Eriksson 1990, Goodell 2003).

To delay or even prevent biodegradation processes, different wood protection systems are available. There is today an increasing demand for wood preservative methods that are based on technologies with low environmental impact. Wood modification involves the action of a chemical, biological or physical agent upon the material, resulting in increased durability (Hill 2006). In contrast to treatments with traditional wood preservatives, where the decay resistance is caused mainly by the toxicity of the chemicals added, little is known about the mode of action of modified wood. Furfurylation of wood is a chemical modification where furfuryl alcohol (FA) penetrates into the wood cell wall, polymerizes *in situ*, resulting in a permanent swelling of the wood cell wall (Goldstein 1955, 1960, Stamm 1977). It has been shown that furfurylation of wood leads to higher durability against biodegradation (Lande *et al.* 2004) and a low environmental impact (van Eetvelde 1998, Lande *et al.* 2004a, 2004b, Pilgård *et al*. 2010a, 2010b).

UV microspectrophotometry (UMSP) is an established analytical technique that enables direct imaging of lignin distribution and lignin modification (biodegradation, delignification) within individual cell wall layers (Fergus *et al.* 1969, Scott *et al*. 1969, Saka *et al*. 1982, Fukuzawa 1992, Koch and Kleist 2001, Koch and Grünwald 2004, Rehbein and Koch 2011, Koch and Schmitt 2013). Rehbein and Koch (2011) detected topochemically the first signs of lignin modification by the brown rot fungus *Antrodia vailantii* in the S2 layer in *Pinus sylvestris* already after three days of incubation.

The aim of this study was to develop a method to investigate furfurylated *Pinus radiata* in order to gain a better understanding of the furfuryl alcohol polymerization process in the wood cell wall and to be able to detect and localize early signs of brown rot degradation.

EXPERIMENTAL

Sample preparation

Small blocks (1.5 x 1.5 x 5 mm) of furfurylated *P. radiata* sapwood, a research product, were trimmed, leached according to EN 84 (1997) and sterilised by gamma radiation. The decay test (Algeier 2014) was performed according to Rehbein *et al.* (2011). Four samples were placed into each Petri dish in front of the growth front of *Postia placenta* (FRIES), M.J. LARSEN & LOMB. (Stamm FPRL 280) (Figure1). Samples were harvested at 12 different times according to Rehbein *et al.* (2011). For this paper we choose a sample after 21 days of incubation. The benefit with the small sample size is that the complete sample can be embedded and prepared for UMSP investigation in contrast to common the degradation test according Bravery (1979) or DIN CEN/TS 15083-1(2005).

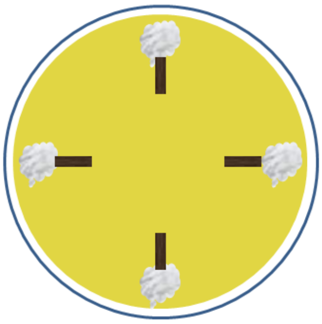

Figure 1: Sample positioning according to Rehbein et al. 2011. The specimens are placed in front of the mycelium of **Postia placenta.**

Light microscopy and scanning UV microspectrophotometry (UMSP)

The samples were dehydrated in a graded series of ethanol, afterwards embedded in epoxy resin according to Spurr (1969), sectioned with a rotary microtome (Leica, RM2265), and transferred to quartz microscopic slides. The semithin sections (1µm), with a size of approximately 0.5 mm², were immersed in a drop of non-UV absorbing glycerine (glycerine/water mixture n_D=1.46) and covered with a quartz cover slip.
Light microscopic analyses were carried out with a microscope (Axiophot, Zeiss) equipped with a digital camera (AxioCam, Zeiss) using AxioVision software.
For the topochemical analyses the sections were placed into a microspectrometer (Zeiss UMSP 80) equipped with a scanning stage. The principle of UMSP investigations is based on the effect that lignin is able to absorb UV light with absorbance maximum in the range of $\lambda_{270-280\,nm}$ (Musha and Goring 1975) displaying a characteristic absorbance spectrum in contrast to the other cell wall compounds cellulose and hemicelluloses. The scan program APAMOS (automatic photometric analysis of microscopic objects by scanning, Zeiss) digitizes square fields of a local geometrical resolution of 0.25 x 0.25 µm² and a photometrical resolution of 4096 greyscale levels. The high resolution (0.25 µm² per pixel) enables a high differentiation of the UV absorbance within the individual cell wall layers. To visualize the absorbance intensities the greyscale levels were converted into 14 basic colours (Koch and Kleist 2001).

RESULTS AND DISCUSSION

Light microscopy

Light microscopy observation of embedded furfurylated *P. radiata* showed intact tracheid tissue with an uneven distribution of polymerized FA located in the cell lumen (brown deposits) (Figure 2a). After 21 days of incubation, no degradation could be seen in the inner parts of the samples and no structural cell wall attacks were detectable (Figure 2b), however the outer parts were degraded. The preparation process of semithin sections of undegraded and degraded furfurylated *P. radiata* caused material depending artefacts (↑). The slices were partly brittle and fragile. One reason could be that FA hinders the epoxy resin impregnation.

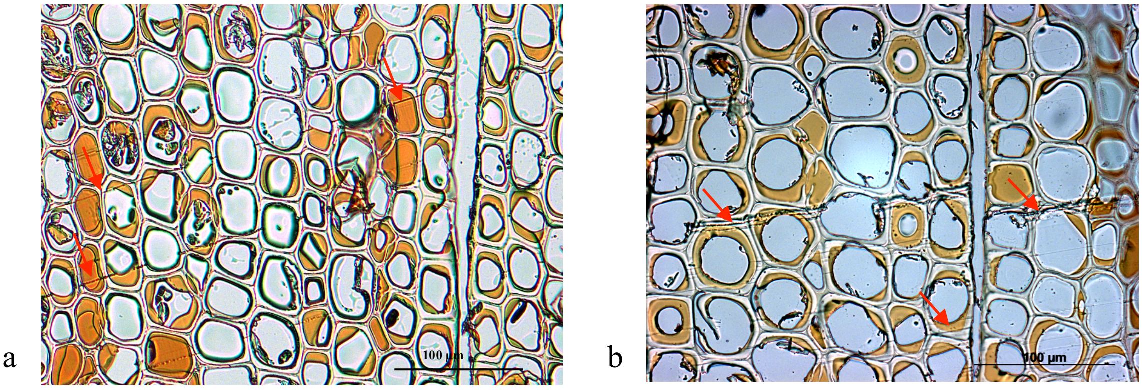

Figure 2: Light microscope cross sections of (a) modified **Pinus radiata and** ***(b)*** **Pinus radiata** ***exposed to*** **Postia placenta (*incubation time:21 days). Both samples showed an uneven distribution of polymerized FA in the cell lumen (brown deposits). The arrows mark preparation artefacts.***

UV microscopic scanning profiles

For the first time, degraded furfurylated wood tissue was investigated by UV microscopy. With *Postia placenta* incubated and undegraded furfurylated *P. radiata* were scanned. The thresholds have been adapted to min 1.00 % and max 67.50 % for all investigated samples, to obtain a suitable evaluation and image generation. Normally the thresholds are set to min 10.00 % and max 80.00 % but with those parameters it was not possible to generate any pictures at all. The intensities of UV absorbance at constant wavelength $\lambda_{280\ \mathrm{nm}}$ are displayed by the different colour pixels. Figure 3 shows UV microscopic scanning profile of undegraded furfurylated *P. radiata*. The control shows a typical lignin distribution profile within the individual cell wall layers. The highest absorbance intensities in the cell wall tissue occur in the area of the compound middle lamella (CML) and the cell corners (CC) as previously described for untreated wood (Scott *et al*. 1969, Fergus *et al*. 1969, Koch and Kleist 2001, Koch and Grünwald 2004). The absorbance values increase from the S3 layer to the area of the CML with approximately abs $_{280\ \mathrm{nm}}$ 1.35 and the CC with values around abs $_{280\ \mathrm{nm}}$ 1.6. UV absorbance intensities of the S2 layers are in the range of abs $_{280\ \mathrm{nm}}$ 1.09–1.48. A spot of high absorbance values in the S2 layer (abs $_{280\ \mathrm{nm}}$ 1.61) could be an indication of an accumulation of polymerized furfuryl alcohol in the cell wall. Polymerized furfuryl alcohol in the cell lumen was detected as overflow (highest absorbance intensity, not shown in the picture).

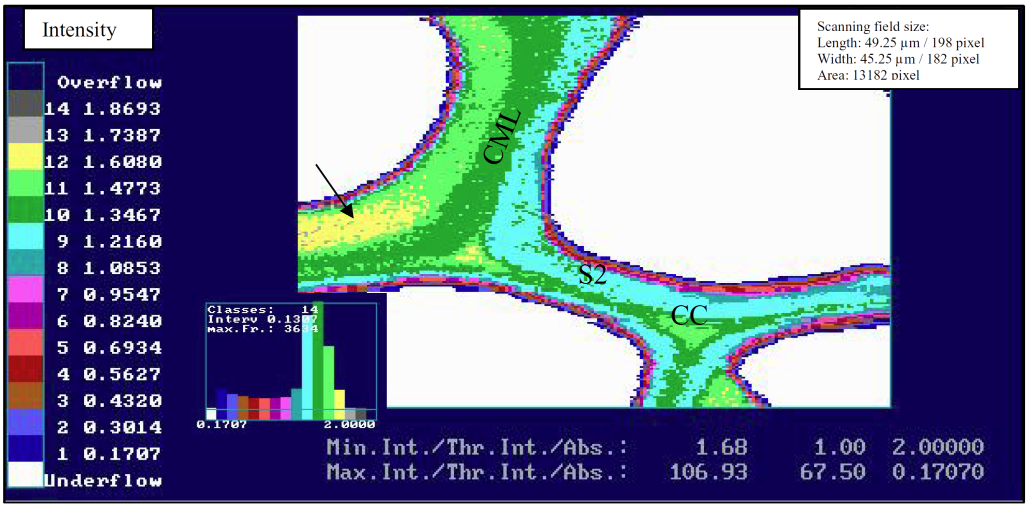

Figure 3: UV microscopic scanning profile of modified* Pinus radiata *with statistical evaluation (histogram). The coloured pixels mark the absorbance intensity at λ $_{280\ nm}$. In the area of the compound middle lamella (CML) and cell corners (CC) are the highest absorbance values in the cell wall tissue. The secondary wall (S2) revealed lower intensities and a spot of high absorbance (↑) that could be an indication of an accumulation of polymerized furfuryl alcohol in the cell wall.

After 21 days of incubation the entire wood tissue of the furfurylated sample appears with lower absorbance values compared to the undecayed control (Figure 4). This decrease in absorbance most likely originates from early fungal degradation processes (Rehbein *et al.* 2011) since no structural cell wall damages could be seen in the light microscope. The polymerized furfuryl alcohol in the cell lumen turned from overflow (not shown in the picture) to absorbance values around abs $_{280\ nm}$ 1.61. The absorbance of the S2 layers shifted from abs $_{280\ nm}$ 1.09–1.48 to abs $_{280\ nm}$ 0.56–0.82 with locally inhomogeneous patterns of lower intensity (figure 4 ↑). The CML is partly not detectable and some small regions are still absorbing (abs $_{280\ nm}$ 0.82). The absorbance values of the CC changed from abs $_{280\ nm}$ 1.48 to abs $_{280\ nm}$ 1.09.

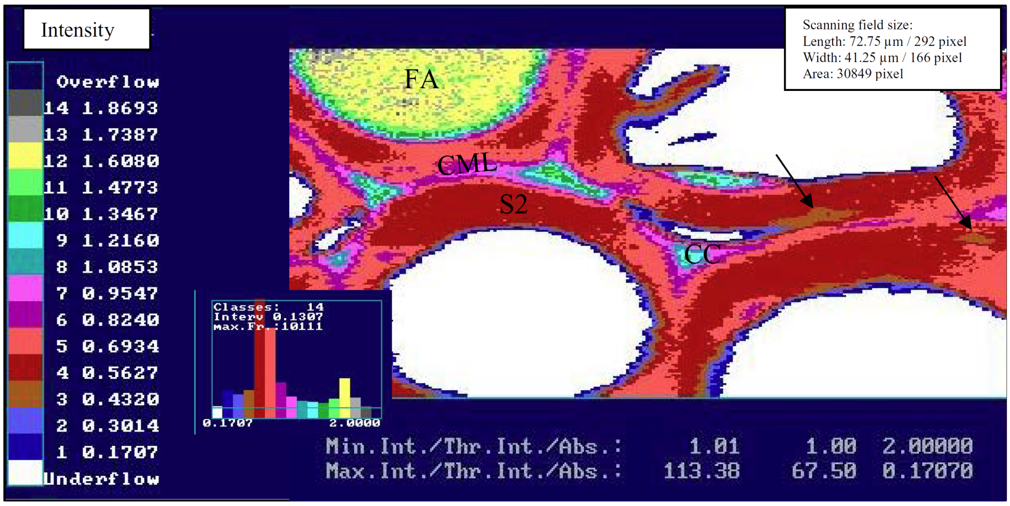

Figure 4: UV microscopic scanning profile at λ $_{280\ nm}$ of modified* Pinus radiata *degraded by* Postia placenta*. The degraded sample revealed a significant decrease of the absorbance intensity form greenish to reddish pixels compared to the control as the statistical evaluation displays (histogram). The secondary wall (S2) revealed lower and locally inhomogeneous pattern of lower intensities (↑) and the onset of lignin modification. The compound middle lamella (CML) is partly degraded, the absorbance values of the cell corners (CC) and the furfuryl alcohol (FA) in the cell lumen decreased.

The topochemical analyses confirm the results from Fackler *et al*. (2010) and Rehbein and Koch (2011) that brown rot degradation starts with a lignin modification through the chelator mediated Fenton degradation in the outermost part of the secondary cell wall and the combined middle lamella (Goodell *et al.* 2003). In the UV microscopic scanning profile this can be seen as a decrease in the absorbance values between figure 3 and 4. In a study performed by Irbe *et al*. (2006) a gradual decrease in lignin absorbance in the CML and CC during brown rot decay could however not be detected. Rehbein *et al.* (2011) noticed an increase in absorbance intensities in the inner parts of the S2 layer after 21 days exposure. One reason for the different results between our study and the study done by Irbe *et al.* could be that in our study only one decay stage was analysed. The thickness of decayed cell walls compared to undecayed cell walls, partial depolymerisation of the native lignin and the changed ratio of lignin to carbohydrates are other factors that also contribute (Irbe *et al.* 2006). Further studies are therefore needed to confirm the results of this paper and another decay test, where more information regarding decay will be gathered, is already in planning.

CONCLUSIONS

After 21 days of incubation, no structural cell wall damages were seen in the light microscope but changes could be detected with the UMSP in the entire cell wall which most likely is the result of early brown rot decay. These results indicate that cellular UV microspectrophotometry is a promising method to study early fungal degradation damages in the cell wall of furfurylated wood. Further degradation studies, where more data regarding decay will be collected, are planned to complement the results from this study.

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SESSION SEVEN

Poster Session 2

Combined Effect of Acetylation and Wax Emulsion on the Physical and Mechanical Properties of Particleboard

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Keywords: acetylation, dimensional stability, mechanical properties, particleboard, wax

ABSTRACT

The effect of the acetylation of wood particles and wax emulsion addition on the physical and mechanical properties of particleboard was investigated. Two different acetylation treatments were applied to wood particles having a moisture content of 4-5% as follows: (1) the wood particles were treated with the acetic anhydride at 100 °C for 1 h and (2) the wood particles were treated with the acetic anhydride (purity 96%) at room temperature (25 °C) for 48 h. After drying of the acetylated wood particles to a moisture content of 4%, the wax emulsion was applied to the wood particles at 0.5 wt% and 1 wt% based on the oven-dry weight of the acetylated wood particles. Single layer particleboards were produced from the pre-treated particles. The acetylation of wood particles significantly improved the water resistance of the particleboards. The TS and WA of the particleboards produced from the acetylated particles improved with increasing amount of wax emulsion. According to the test results, the water resistance of the particleboards can be improved by acetylation of the wood particles at 25 °C for 48 h without decreasing bending properties.

INTRODUCTION

Wood changes dimensions with changing moisture content because the cell wall polymers contain hydroxyl and other oxygen-containing groups that attract moisture through hydrogen bonding. The hemicelluloses are mainly responsible for moisture sorption, but the accessible cellulose, non-crystalline cellulose, lignin, and the surface of crystalline cellulose also play major roles (Rowell 2004).

The chemical modification of wood is a very good alternative to conventional wood preservation methods. Acetylation has received considerable attention - more than any other chemical modification technique known (Kwon *et al.* 2007, Azeh *et al.* 2013). This is method not only protects wood/wood-based products against degradative agents, but also changes the hydrophilic nature of the wood components (cellulose, hemicellulose, and lignin), imbuing hydrophobicity by increasing the acetyl content in the polymers while decreasing their –OH groups (Azeh *et al.* 2013). In many chemical modification reactions the hydroxyl groups play the leading role. Esters are formed by the reaction of wood with carboxylic acids or anhydrides. The acetylation of solid wood, wood fibres, chips, veneers etc. with acetic anhydride have been studied the most and reported by dozens of authors. In this study, the effect of acetylation and wax emulsion on the physical properties of particleboard was investigated.

EXPERIMENTAL DETAILS

Raw materials

Wood particles were supplied from a commerical particleboard plant in South Korea. Wood wastes obtained from construction and furniture were converted into the particles in the plant. The average moisture content of the wood particles prior to the production of the boards was 3-4% based on the oven-dry weight of the wood particles. Urea-formaldehyde resin (solid content 60 wt%) was obtained from the particleboard plant in South Korea. Acetic anhydride ($(CH_3CO)_2O$), having a molecular weight of 102.1 and a purity of 96%, and wax emulsion having a solids content of 40 wt% were supplied from a chemical company in South Korea

Acetylation of wood particles

The wood particles were treated with the liquid acetic anhydride at room temperature (25 °C) for 48 h or heated at 100 °C for 1 h (Fig. 1). The particles pre-treated at 100 °C for 1 h had a 4.75% weight percent gain (WPG) while the particles pre-treated at room temperature for 48 h had a 3.58% WPG. After the acetylation process, the wood particles were dried until air-dry on the floor (outside). After drying of particles, the wax emulsion was applied to the wood particles at 0.5 and 1.0 wt% based on the oven-dry weight of the wood particles. The wood particles were dried to 2-3% moisture content before the production of single layer particleboards.

Figure 1: Acetylation of wood particles. A: heating at 100 °C for 1 h,
B: room temperature (25 °C) for 48 h

Production and testing of particleboards

The wood particles were homogeneously mixed by hand and placed in a plastic container. The liquid UF resin, 10 wt% based on the oven dry weight of wood particle, was then sprayed on the particles with pneumatic nozzles and blended by hand at ambient temperature to obtain a homogenized mixture. Following the resin application, the mixed wood particles were weighed and distributed evenly by hand into a 290 mm x 290 mm forming box. Release agent was used to avoid direct contact of the wood particles with the steel caul plates during heating and pressing. To reduce the mat height and to densify the mats, they were subjected to a cold-press. The single layer mats were subjected to the hot-pressing process. The mats were pressed into 10 mm thick boards using 3.0 N/mm^2 at a 180 °C press temperature and 5 min press time. The boards were then trimmed to a final size of 280 mm x 280 mm after the cooling process. A total of 27 composite particleboards, 3 for each type of formulation, were produced (Table1). Prior to testing the specimens were conditioned to constant mass at a temperature of 23 °C and a relative humidity of 65%. Some physical properties; density, moisture content, water absorption (WA) and thickness swelling (TS) as well as mechanical properties; modulus of rupture (MOR), modulus of elasticity (MOE) and the internal bond (IB) strength of the particleboards produced were determined according to Korean Standard (KS) F 3104 (2002). Six samples were taken for each test.

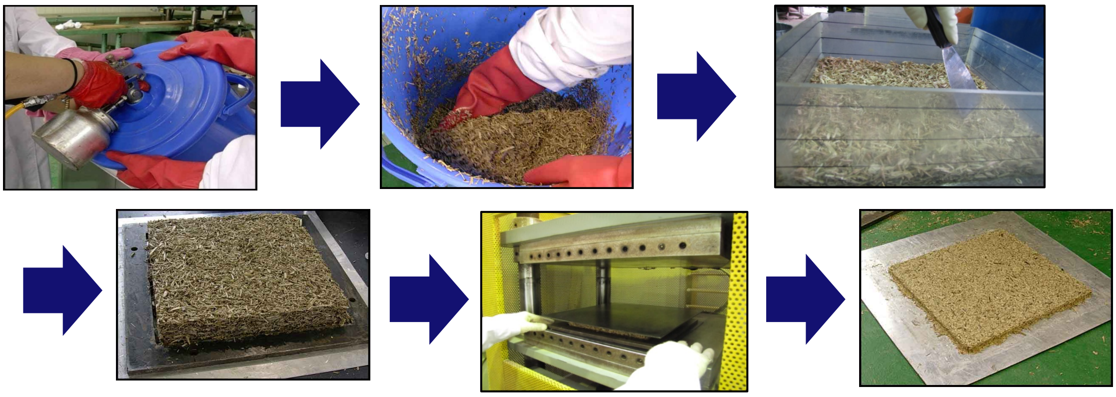

Figure 2. The production process of the single-layer composite particleboards

RESULTS AND DISCUSSION

The physical and mechanical properties of the particleboards are presented in Table 1. The TS and WA of the particleboards produced from the control and acetylated particles considerably decreased with the increasing amount of the wax emulsion (Table 1). For example, as the amount of wax emulsion increased to 1 wt%, the TS and WA of the control particleboards decreased from 41.3 to 25.4% and from 68.8 to 49.7%, respectively. The MOR and MOE of the control particleboards improved as the amount of the wax increased to 0.5 wt% (panel types A and B). However, a further increment in the wax content decreased the MOR and MOE. The MOE (3546 N/mm^2) of the particleboards (type C) produced with 1 wt% wax was higher than that (3316 N/mm^2) of the particleboard without wax (type A). The IB strength of the control particleboards decreased with increasing amount of wax emulsion.

Table 1: Physical and mechanical properties of particleboards

Panel type	Pre-treatment	Wax addition (wt %)	Physical properties				Mechanical properties		
			Density (g/cm^3)	MC (%)	TS (%)	WA (%)	MOR (N/mm^2)	MOE (N/mm^2)	IB (N/mm^2)
A	Control	0	0.84	3.75	41.3	68.8	22.0	3316	0.93
B		0.5	0.87	3.37	27.4	52.6	22.8	3943	0.61
C		1	0.86	3.87	25.4	49.7	19.8	3546	0.57
D	Acetylation of particles at 100 °C for 1 h	0	0.81	3.24	13.2	40.2	12.1	2257	0.32
E		0.5	0.81	3.20	7.2	30.0	7.9	1785	0.23
F		1	0.81	3.81	6.6	23.6	7.4	1740	0.22
G	Acetylation of particles at 25 °C for 48 h	0	0.88	3.33	31.8	55.6	22.4	3443	0.74
H		0.5	0.86	3.30	23.2	46.9	19.0	3247	0.67
I		1	0.89	3.24	16.5	28.3	18.1	3467	0.51

MC: moisture content. TS: thickness swelling (24-h). WA: water absorption (24-h). MOR: modulus of rupture. MOE: modulus of elasticity. IB: internal bond strength.

The TS and WA of particleboards produced from the acetylated wood particles at 100 °C for 1 h were significantly lower than those of the particleboards produced from acetylated wood particles at 25 °C for 48 h. As the wax amount increased from 0.5 to 1 wt%, the average TS value of the particleboards produced from the acetylated wood particles at 100 °C for 1 h slightly decreased (7.2 to 6.6%). However, the average TS value of the particleboards produced from the acetylated wood particles at 25 °C for 48 h decreased considerably (23.2 to 16.5%) as the wax amount increased from 0.5 to 1 wt%.

The mechanical properties of the particleboards were significantly decreased by the acetylation of wood particles. The MOR, MOE, and the IB strength of particleboards produced from the acetylated wood particles at 100 °C for 1 h were significantly lower than those of the particleboards produced from the acetylated wood particles at 25 °C for 48 h. In particular, the MOR and MOE of the particleboards produced from the acetylated wood particles at 100 °C for 1 h significantly decreased as the wax content increased to 0.5 wt%. However, the bending properties of the particleboards decreased very slightly as the wax content increased from 0.5 to 1 wt%. Similar results were observed for the IB strength. The bending properties of particleboards (type G) produced from the acetylated wood particles at 25 °C for 48 h were slightly higher than those of the control particleboards (type A). The MOR of the particleboards produced from the acetylated wood particles at 25 °C for 48 h decreased with increasing wax content but the MOE was not affected by the addition of 1 wt% wax (type I).

CONCLUSIONS

The results of the study showed that the acetylation of wood particles significantly improved the water resistance of the particleboards. The TS and WA of the particleboards produced from the acetylated particles at 100 °C for 1 h were significantly lower than the particleboards produced from acetylated particles at 25 °C for 48 h. The TS and WA of the particleboards produced from the acetylated particles decreased with increasing amount of wax emulsion. Among the treated particleboards, the lowest decrease in the mechanical properties was found in the particleboards produced from the acetylated particles at 25 °C for 48 h. Based on the finding obtained from the present study, it can be said that the water resistance of the particleboards can be improved by acetylation of the wood particles at 25 °C for 48 h without decreasing bending properties.

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Impact of Wood Species on Furfuryl Alcohol Modification Studied by DSC

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Keywords: differential scanning calorimetry, furfuryl alcohol modification, wood species, pH values

ABSTRACT

The furfuryl alcohol modification of wood is a well-known process for wood property enhancement leading *e.g.* to increased durability and dimensional stability (*e.g.* Epmeier *et al.* 2004, Esteves *et al.* 2011, Lande *et al.* 2004). Previous differential scanning calorimetry (DSC) studies on furfuryl alcohol impregnated maple veneer (*Acer* spp.) suggested a close relationship between curing temperatures and durations and the amount of maleic anhydride used for starting furfuryl alcohol polymerisation at elevated temperatures (Herold *et al.* 2013). In addition to these results and in order to assess the impact of different wood species with varying pH on furfuryl alcohol polymerisation temperature and duration, the present DSC experiments were carried out on various wood veneer specimens impregnated with furfuryl alcohol. Pure furfuryl alcohol has a single endothermic peak at 151 °C attributed to the evaporation of furfuryl alcohol. On the other hand furfuryl alcohol and 10-wt-% maleic anhydride led to a single exothermic peak at 116°C. The impregnated veneers also exhibited exothermic peaks but at a different temperature for each wood species. European maple (*Acer* spp.) has an exothermic peak at 123 °C and the pH value of its cold/hot water extract is 5.4. European oak (*Quercus* spp.) has an exothermic peak at 113 °C and the pH value of the corresponding water extract is 5.3.

INTRODUCTION

Wood modification with furfuryl alcohol is a well-known process used to improve particular wood properties. The polymerization of furfuryl alcohol inside wood reduces the equilibrium moisture content and increases dimensional stability and durability (Esteves *et al.* 2011). Also, furfuryl alcohol modification increases hardness, resistance to microbial decay and insect attack, modulus of rupture (MOR) and modulus of elasticity (MOE) (Lande *et al.* 2004).

Furfuryl alcohol modification is an acid catalysed reaction. In the modification of wood, furfuryl alcohol polymerisation is initiated by maleic anhydride and elevated temperature.

Previous researchers have claimed that maleic anhydride has a great impact on the polymerization reaction (Wewerka 1968). Increased maleic anhydride content in the impregnation solution activates more furfuryl alcohol, leading to a lower curing temperature (Herold *et al.* 2013).

Wewerka (1968) claimed a correlation between the pH value and the initial reaction mechanism of furfuryl alcohol polymerization. Wood contains extractives formed from a large number of different compounds that can be extracted by different polar and non-polar solvents (Fengel and Wegener 2003). Among the extractable substances are water-soluble carbohydrates and inorganic compounds, *e.g.* aldehydes, alcohols, phenols, carboxylic acids, carbohydrates which can be solved by hydrolysis (Fengel and Wegener 2003). As a result, the pH value of wood extracts differs between species. Thus wood species with lower pH values have potentially more protons available to initiate furfuryl alcohol polymerization.

DSC measurements monitor the heat effects associated with physical processes and chemical reactions as a function of temperature. The present DSC experiment was conducted to investigate the change in curing temperature of furfuryl alcohol modification in relation to different pH values and the availability of protons in various specimens. As a result, the process parameters of furfuryl alcohol polymerization in various wood species were determined and adapted *e.g.* curing temperature.

EXPERIMENTAL

Preparation of specimens

The specimens were cut from various commercial wood veneers. The wood species used were European maple (*Acer* spp.), ash (*Fraxinus excelsior* L.), European oak (*Quercus* spp.), and larch (*Larix decidua* Mill.). The thickness of the sliced veneer sheets used was 0.6 to 0.7 mm. For comparable size, the specimens were cut into 3mm discs with punch pliers and then halved by knife into semicircles. Two specimens of each wood species were cut from the same veneer sheet.

The samples were dried at 70°C to constant weight. For impregnation, 10 wt.-% maleic anhydride (Merck Schuchardt OHG) was dissolved in neat furfuryl alcohol (>98%, Merck Schuchardt OHG). The specimens were impregnated for 30 min at 100 mbar. In order to allow the maximum uptake of furfural alcohol into the cell walls, the impregnated veneer specimens were stored in the impregnation solution under atmospheric pressure for 48 h.

DSC measurement

For the DSC measurements, the impregnated specimens and impregnation liquids were enclosed in standard aluminum DSC crucibles with a pierced lid. The measurements were performed using a Netzsch DSC 204 F1 Phoenix instrument. A heating ramp of 10 °C/min from 20 to 200 °C was applied in order to investigate furfuryl alcohol curing. All experiments were carried out under a nitrogen atmosphere with a purge gas flow of 100 ml/min.

pH values

Two water extracts were prepared from each unmodified wood veneer to determine the pH of the corresponding extracts. For the cold water extracts, 2.5 g of veneer were cut into small chips and extracted in 50 ml distilled water for 30 min at room temperature. For the hot water extracts, 2.5 g veneer were cut into small chips and extracted in 50 ml distilled water for 30 min at 100 °C. Subsequently, the pH values of the cold and hot water extracts were determined using a pH meter from WTW (inoLab pH Level 1).

Weight percentage gain (WPG)

The mass uptake of each veneer during the furfurylation process and the loss during DSC measurement was determined as WPG using Eqn. 1.

$$WPG = \frac{(W_t - W_u)}{W_u} * 100 \qquad (1)$$

where WPG is the weight percentage gain of the sample after impregnation *resp.* after DSC measurement [%]. W_t is the weight of the sample after impregnation, respectively after DSC measurement [g]. And W_u is the weight of the absolutely dry sample [g].

RESULTS AND DISCUSSION

In the present study, the pH value of each veneer used was determined by water extraction. For comparison of the specimens the WPG were calculated after impregnation with furfuryl alcohol and after DSC measurement (Table 1). Also the exothermic peak temperature was determined to show displacement of the exothermic peak (Table 1).

Table 1: Results

Species	pH value[1]	pH value[2]	WPG [%][3]	WPG [%][4]	T [°C][5]
Acer spec.	5.4	5.1	181.0	124.0	123.0
			182.5	117.5	123.5
Fraxinus excelsior L.	5.9	6.1	140.1	93.9	113.7
			150.0	99.1	112.3
Quercus spec.	5.3	4.7	183.5	133.1	111.3
			150.8	103.1	109.1
Larix decidua Mill.	4.7	4.6	180.1	120.8	120.9
			207.5	141.8	119.4

[1]pH value (cold water extraction), [2]pH value (hot water extraction), [3]WPG after impregnation, [4]WPG after DSC, [5]Peak temperature

DSC measurement of the impregnation liquid (10 wt.-% maleic anhydride dissolved in furfuryl alcohol) led to a single exothermic peak at 116 °C. The peak temperature of furfuryl impregnated European maple is displaced to an exothermic peak at 123 °C. In contrast European oak exhibits an exothermic peak at 113 °C (Figure 1). The water-extracts of both wood species showed different pH values (European maple 5.4, European oak 5.3 (Table1)). Thus European oak seems to accelerate the reaction compared to the neat impregnation solution. Here, the polymerization of furfuryl alcohol reaches a maximum at a lower temperature. In contrast, European maple seems to shift furfuryl alcohol polymerization to higher temperature.

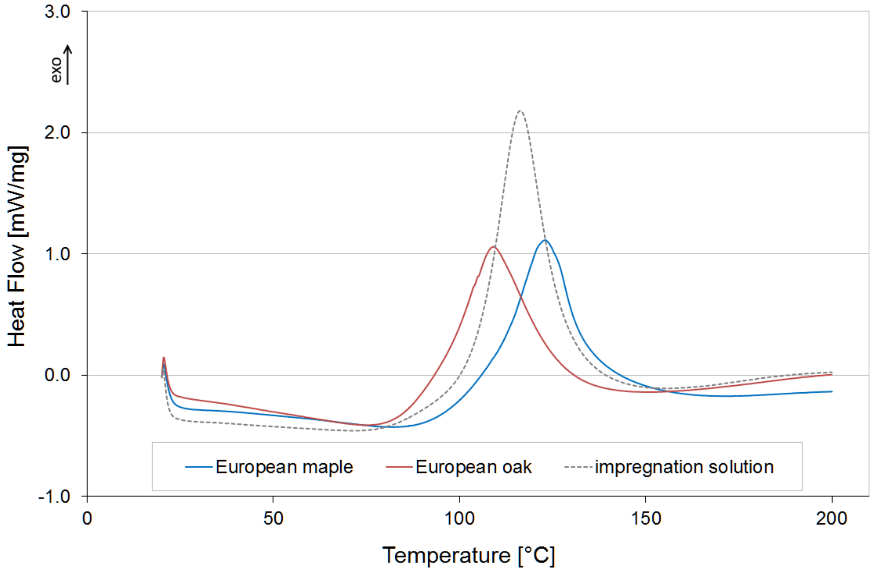

Figure 1: DSC thermogram of impregnated European maple, European oak, and impregnation liquid

In commercial veneer production processes, most wood logs undergo a pre-treatment. In general, logs for veneer slicing are cooked or steamed for several hours (Kollmann 1962). During this process, some wood components are solved and washed out. Therefore, the pH value of the veneer produced can be different to that of the logs before production. Thus, the pH values of extracts from veneer may differ from the values found in the literature.

CONCLUSIONS

Each wood species has a certain pH value. The polymerization of furfuryl alcohol in wood can be initiated by the temperature-induced reaction of maleic anhydride with furfuryl alcohol. If additional proton sources are available, furfuryl alcohol polymerization might be shifted towards a lower temperature or intensified. The present study shows a large variation in the polymerization temperature of furfuryl alcohol inside different wood veneer species. The results shown in Figure 1 do not show a clear correlation between pH values and the exothermic peak temperature of furfuryl alcohol polymerization. It could not be clearly proven whether the pH value of various wood species influences the furfuryl alcohol polymerization temperature or whether other wood features influence it.

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Gluing Melamine Treated Wood – Apparent and Actual Bonding Performance

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Keywords: adapted specimen geometry, bonding performance, melamine treatment, polyurethane adhesive, tensile shear strength

ABSTRACT

The scope of the study was to gain knowledge on the bonding performance of modified wood. Untreated and melamine treated beech (*Fagus sylvatic*a L.) and Radiata pine (*Pinus radiata* D. Don) wood was used. A one-component polyurethane adhesive was utilized to manufacture lap joints. To overcome the problem of invalid specimens, which cannot be evaluated, the specimen geometry referred to in DIN EN 302-1 (2013) was adapted. The lap joints were exposed to one of two storage conditions (A1 and A2), according to the standard. Subsequently, tensile shear strengths as well as wood failure percentages were determined. The dependency of the bonding performance on the elasto-mechanical properties of the adherent substrate are discussed. Melamine treated wood reveals both high tensile shear strengths and high wood failure percentages especially when adapted specimen geometries are applied. The higher bonding strength of the melamine treated wood is explained by discussing the influence of the tensile modulus of the substrate, which actually influences bonding strength positively, and specimen geometry, which only apparently enhances the bonding strength, or tensile shear strength, of bonded lap joints.

INTRODUCTION

Generally, standardized testing methods require the utilization of unmodified beech wood for quantifying the bonding strength of adhesive systems. However, in many aspects, the bulk and surface characteristics of modified wood clearly differ from untreated material. Consequently, both the intrinsic mechanical properties as well as adhesion are directly influenced by wood modification. Hence, the evaluation of bonding performance can only be accomplished by adapting commonly used testing methods dependent upon material properties. In the present study the bonding performance of untreated and melamine treated beech and Radiata pine was evaluated by applying testing methods in accordance with DIN EN 302-1 (2013) with the adaptation of the specimen geometry. In order to evaluate the resulting strain distribution of the adapted geometry, the deformation of selected samples was measured by means of electronic speckle pattern interferometry.

EXPERIMENTAL

The investigations were carried out using untreated as well as melamine treated beech wood (*Fagus sylvatica* L.) and Radiata pine (*Pinus radiata* D. Don) as adherents. For the melamine modification a melamine solution with 30 and 20 % solid content (Madurit MW840 75WA), respectively, supplied by INEOS Melamines, Germany, was used to impregnate the boards (1000 x 150 x 30 mm³). With a maximum temperature of 90 °C accompanied by steam injection, curing was accomplished in a high-temperature dryer for about ten days resulting in Weight Percentage Gains of approx. 25 % and 19 %, for the 30 and 20 % melamine solutions respectively. Based on DIN EN 302-1 (2013) the tensile shear strength of bonded specimens was defined. Two geometries of specimens were investigated. In one the standard lamella thickness of 5 mm was used and in the other an adapted lamella thickness of 10 mm was used (Figure 1).

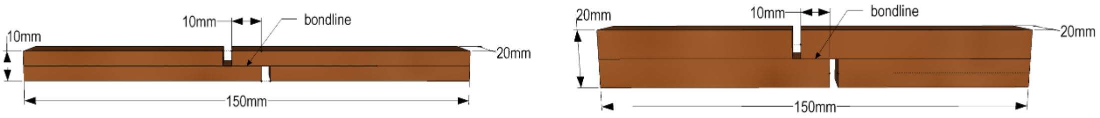

Figure 1: Specimen geometry for quantifying tensile shear strength of bonded lamellas; Standard geometry in accordance to DIN EN 302-1 (2013) (left); Adapted geometry (right).

For bonding a one-component polyurethane resin (Jowapur 686.60), supplied by Jowat AG, Germany, was employed. All bonding processes were conducted according to the manufacturer’s recommendations. The PUR adhesive was applied manually to one side amounting to about 250 $g*m^{-2}$. The open and closed assembly time took 15 min, respectively. The adhered boards were pressed for six hours at room temperature and stored for four weeks. Before testing, the specimens were exposed to one of two conditioning sequences in accordance with DIN EN 15425 (2008): A1 (20 °C / 65 RH) and A2 (4 d submersion in water). Both types of specimens were stressed along the grain to failure at an elongation rate of 1 $mm*min^{-1}$ in a Zwick/Roell universal testing machine (10 kN load cell). Beside the tensile shear strength, the area of wood failure on the bonding surface was calculated. Additionally, 3D full field deformation of selected beech specimens were measured by means of electronic speckle pattern interferometry (ESPI, Q300 from Dantec-Ettemeyer, Germany) and subsequently strain distribution was identified by ISTRA processing software (Dantec-Ettemeyer, Version 3.3.12, 2001). Müller *et al.* (2005) describe both the method and analysis in detail.

RESULTS AND DISCUSSION

The tensile shear strength of PUR-bonded beech and pine wood specimens displayed a dependence on the specific preliminary storage conditionings (Figure 2). Generally the quality control of adhesively bonded joints can be based on criteria like tensile shear strength and wood failure percentage (WFP). According to the results, PUR-bonded and melamine treated joints, exhibit higher tensile shear strengths than untreated adherents, except for the case of melamine treated pine after normal conditioning, where a significant reduction in strength is noticeable. In this case both the wooden material and the melamine treatment itself seem to negatively influence the adhesion properties of Radiata pine. Melamine treated specimens fulfil normative thresholds when being tested wet. It is assumed that this increase of strength is influenced strongly by a combination of material properties: Firstly, under wet conditions melamine treated wood exhibits higher shear strength than untreated wood (own unpublished results). Secondly, the melamine treatment enhances the dimensional stability reducing swelling and shrinking reactions (Mahnert 2013). In almost all circumstances the melamine treatment results in an increase of WFP. It becomes obvious that bonding strength is actually positively influenced by the melamine treatment.

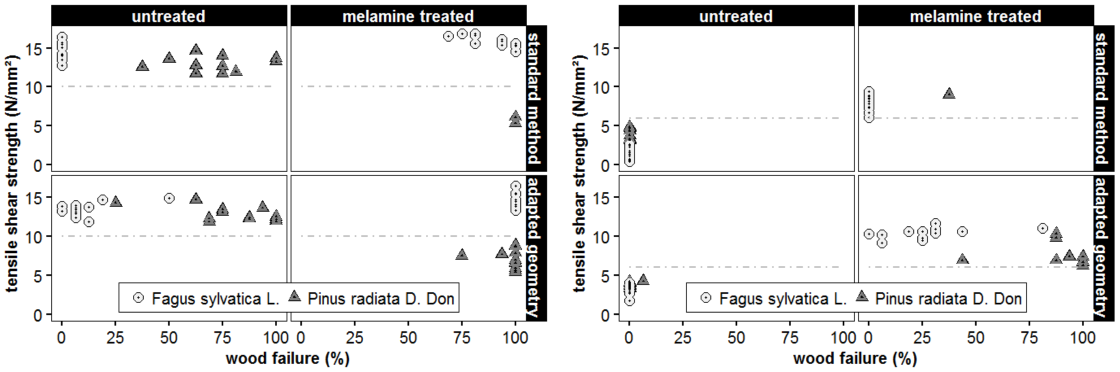

Figure 2: Tensile shear strength of bonded specimens subsequent to storage conditions; A1: 20 °C and 65 % RH (left), A2: submersion into water (right). Dot-dashed line represents normative thresholds.

Adapting the geometry of standardized specimens in the form of increasing lamella thicknesses leads to both higher shear strength and higher WFP especially under wet conditions (Figure 2). Gindl-Altmutter *et al.* (2012) discussed the effect of varying specimen geometry on strength properties using Volkersen´s shear lag model. In accordance with Volkersen (1938), the impact of stress concentrations within the bondline can be estimated (Eqn. 1).

$$\frac{\tau}{\tau_a} = \sqrt{\frac{GL^2}{2E_s t\eta}} \qquad (1)$$

τ is the local peak shear stress within a bondline, whereas τ_a is the average shear stress within a lap joint. G is the shear modulus of the adhesive. The tensile modulus of the substrate is defined by E_s. L quantifies the overlap length of the lap joint, t is the thickness of the bonded substrate and η is the thickness of the adhesive layer. With increasing tensile modulus and substrate lamella thickness, the peak stresses within the bondline decrease (Stoeckel *et al.* 2013).

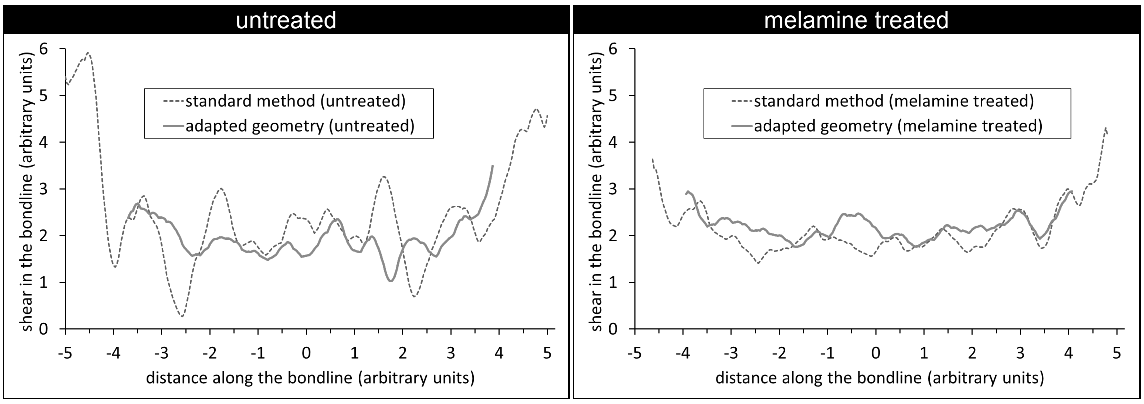

Figure 3: Shear strain distribution along the bondline of beech wood joints being tested subsequent to a normal climate conditioning sequence (A1).

In this study it was also proven experimentally that the shear strain distribution along the bondline varies considerably depending on both wood modification and thus modulus of the adherent and specimen geometry (Figure 3), apparently influencing bonding strength. It is assumed that the modulus of wet untreated wood is much lower than that of melamine treated wood. As a consequence, the difference in peak stresses between the untreated and melamine treated wood within the bondline of the wet specimens should be even higher than presented in the conditioned specimens (***Figure***). Furthermore, in the current study it could also be verified that the number of valid specimens being tested increases significantly when utilizing the adapted specimen geometry. Hence the labour-intensive effort of sample production could be distinctly reduced by focussing on the adapted geometry.

CONCLUSIONS

Within a bondline, the shear strain distribution varies considerably depending on both wood modification and specimen geometry. Melamine treatment enhances dimensional stability and tensile modulus and thus the actual bonding performance. As a result, the bondline of the PUR-bonded melamine treated wood in combination with a thicker specimen geometry experiences reduced peak stresses and hence exhibits higher bonding strengths. Utilization of the adapted specimen geometry is recommended due to the considerably higher number of valid specimens. However, an evaluation of bonding performance following DIN EN 302-1 (2013) must only be based on tests utilizing the same specimen geometry to avoid deficient interpretations.

ACKNOWLEDGEMENTS

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Crack Formation During Oil-Heat-Treatment in Relation to the Initial Moisture Content

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Keywords: oil-heat-treatment, crack formation, moisture content, SEM

ABSTRACT

In this study crack formation in spruce (*Picea abies*), hornbeam (*Carpinus betulus*) and tree of heaven (*Ailanthus altissima*) wood during Oil-Heat-Treatment (OHT) was investigated. The wood species investigated were selected and targeted according to the anatomical structure, for the reason of having a softwood, a ring porous hardwood and a diffuse porous hardwood. The treatment temperature was 200°C and the treatment time was 6 hours. The samples were put directly into the hot oil, thus the treatment was a relatively intensive method, as no preheating or curing was made. The specimens were differentiated into three groups according to the initial moisture content (before heat treatment). The moisture contents were 0%, ~12% and green state (over fibre saturation point). Crack formation was investigated with the scanning electron microscope (SEM) imaging technique. In the case of specimens heat treated in the green state, the cracks could be seen well with the naked eye. The role of the initial moisture content was clear; as it increased the number and dimensions of the cracks also increased. In case of 0% initial moisture content only a little damage with few and very small cracks were observed, and a little more and larger cracks in the case of ~12% initial moisture content. In case of wood in the green state the cracks were large and very frequent. The cracks occurred mostly next to the rays and along the middle lamellae in the case of all wood species and initial moisture contents.

INTRODUCTION

It is important to know the effect of initial moisture content on crack formation, because micro-cracks influence the strength properties and the quality of heat treated wood. As softwoods and hardwoods have different cell types and structure, the effect of heat treatment is different in them as well (Boonstra *et al.* 2006a-b). As the initial moisture content is a process parameter which can be influenced before heat treatment, it is important to know how it affects the wood quality during heat treatment. In this study a relatively intensive heat treatment method - Oil-Heat-Treatment - is described without preheating and conditioning of the material during the treatment. According to earlier investigations (Bak *et al.* 2009) poplar and beech wood, for example, did not show cracks or deformations as a result of this treatment method but, on the other hand, turkey oak or ash wood showed several cracks. Anatomical structure, cell types present in the wood species and the presence of tyloses have a large effect on crack formation during heat treatment. In this study crack formation as a result of heat treatment in different wood species having different initial moisture contents was investigated with scanning electron microscopy (SEM).

EXPERIMENTAL

Norway spruce (*Picea abies*), hornbeam (*Carpinus betulus*) and tree of heaven (*Ailanthus altissima*) wood was oil-heat-treated (OHT) in linseed oil. The dimensions of the treated samples were 18×40×220 mm (T×R×L). The treatments were performed at a temperature of 200°C, for 6 hours duration. Samples with different initial moisture contents were heat treated. The initial moisture contents investigated were 0% (absolute dry state), ~12% (air dry state) and above fibre saturation point (green state). To reach the absolute dry state, samples were put in a drying chamber at 103±2 °C until reaching constant weight. To reach the air dry state, the samples were put in a climatic chamber at conditions of T=65°C and φ=65% until reaching constant weight. To simulate the green state, samples were put under water for 10 days.

The presence and location of cracks were investigated with a scanning electron microscope. The device used was a Hitachi S3400 scanning electron microscope. Specimens were scanned under vacuum pressure of 70 bar and an accelerating voltage of 25 kV. The surfaces were not gold coated with a sputter-coater machine before the imaging. After OHT the samples were cut to get clear anatomical surfaces (tangential, radial and cross section), and to make visible the internal cracks in the wood tissue.

RESULTS AND DISCUSSION

In the case of specimens heat treated in the green state, the cracks could be seen well with the naked eye (Figure 1) The reason for this is the intensive heat transfer to the wood. During the intensive heat treatment the steam pressure increases quickly in the lumens of the wood. As parenchyma cells have the weakest cell wall in the structure of the wood, the cracks occur in the rays which are visible as radial cracks. Additionally, deformation of the cross-sections occurred during heat treatment, as the edges of the cross-sections were not straight after the treatment, but rather curved. Usually these deformations occurred in the case of the hardwoods (hornbeam and tree of heaven) investigated and they were not present in the case of spruce.

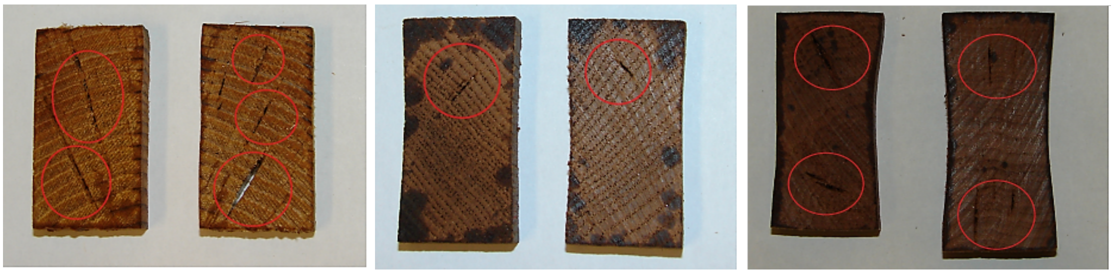

Figure 1: Radial cracks and deformations on the cross section of spruce (left), tree of heaven (middle) and hornbeam (right)

In the case of spruce, micro-cracks were formed in a large quantity near the annual ring border and almost only in the radial direction (Figure 2). This is because of the big differences between the mechanical properties and wood-water relations (shrinkage, diffusion) of the earlywood and latewood, originating from differences in the cell structure. Therefore, the annual ring border acts as a stress inducing location in the wood structure during the heat treatment. Most of the micro-cracks could be observed next to the rays. As the moisture/water leaves the wood in the form of steam during heat treatment, the steam pressure increases rapidly in the lumens. The reason for the large number of cracks in this region is the thin and weak cell wall of the ray parenchyma cells, which can collapse more easily compared to the tracheid cells. On the other hand, the collapses often occurred between the cells along the middle lamellae, which is also a weak point in the wood structure.

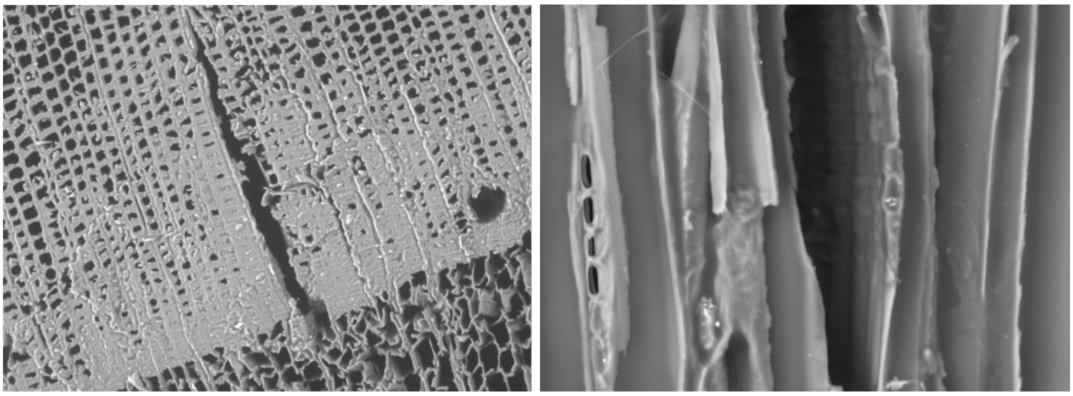

Figure 2: SEM images from cracks of spruce cross section (left) and tangential surface (right)

In the case of the tree of heaven the cracks occurred almost only in the radial direction as well. Most of the micro-cracks could be observed next to the rays or in the rays between the single ray cells, as was also observed in spruce (Figure 3). Several cracks were continued from the rays into the base tissue (libriform fibers) of the wood as well. In the vessels only a few and small cracks occurred during the treatment. Tree of heaven has large and open vessels (without tyloses), thus the steam formed during heat treatment from the moisture in the cell walls and lumens can easily leave the wood tissue. Therefore the stresses induced by the increased steam pressure are lower in the vessels as well. The cracks often occurred between the cells along the middle lamella as in spruce.

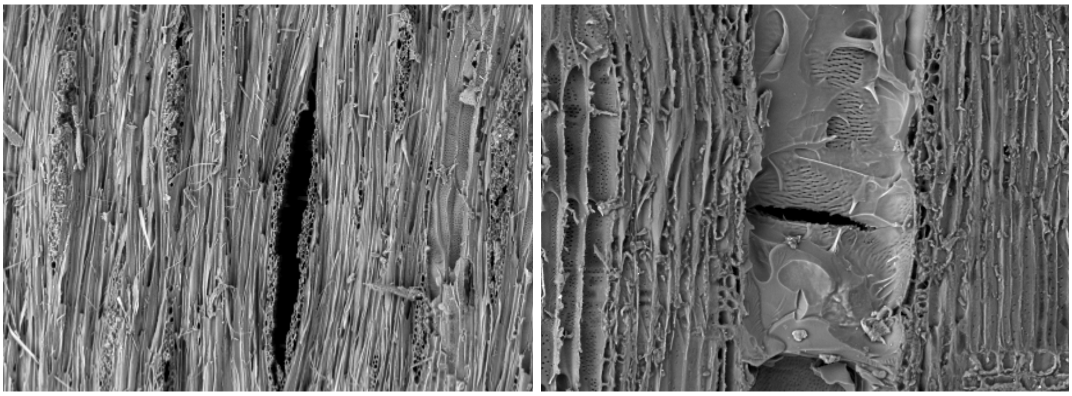

Figure 3: SEM images from cracks of tree of heaven tangential surface (left) and radial surface (right)

In the case of hornbeam as well, the cracks almost only occurred in the radial direction. Large cracks could be observed, and the cracks were located mostly in the cumulative rays between the single cells, along the middle lamella (Figure 4). Damage to the vessels could not be found.

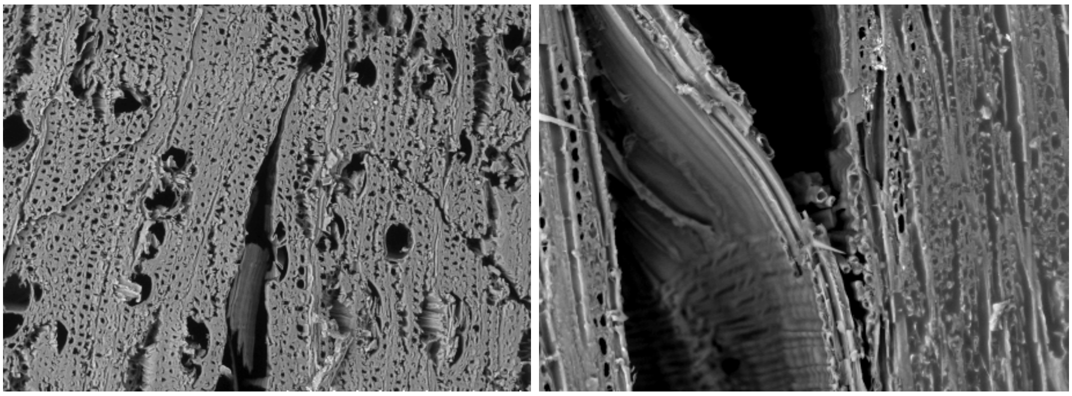

Figure 4: SEM images from cracks of hornbeam cross section (left) and tangential surface (right)

CONCLUSIONS

The role of the initial moisture content was clear; as it increased so too did the number and dimensions of the cracks. In the case of 0% initial moisture content only a few and very small damages were observed, and a little more and larger cracks in the case of a ~12% initial moisture content. In the case of an initial moisture content in the green state, the cracks were large and very frequent. The cracks mostly occurred next to the rays and along the middle lamellae in the case of all wood species and initial moisture contents.

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Emissions from Bio-Based Building Products

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Keywords: corrosion, emissions, volatile organic compounds

ABSTRACT

In this study the applicability of bio-based building materials, for sensitive environments, such as hospitals, schools and museums, in particular, was investigated. For this, specimens of fresh-sawn oak *(Quercus robur),* ash *(Fraxinus excelsior)* and alder *(Alnus glutinosa, (L.) Gaertn.)* were pre-treated with a buffer solution and heat-treated at low temperatures under vacuum conditions. The measured quantities of volatile organic compounds (VOC) were characterised by gas chromatography (GC) in combination with mass-spectroscopy (MS) and high-performance liquid chromatography (HPLC). In addition several field trials and laboratory exposure tests were performed to investigate the corrosive characteristics of the gases. Compared to untreated samples, the formaldehyde and acetaldehyde emissions were lower in the pre-treated samples of ash and alder, whereas they were slightly higher in the pre-treated oak samples. The VOC emissions (aldehydes) were clearly reduced by the applied buffer. The atmospheric corrosion of unstable metals such as lead is strongly accelerated by the availability of water and acetic acid, which is still inherent in the samples and in the atmosphere inside the test vessel. The results imply that acetic acid vapour, due to the availability of water, is a very important corrosive agent for lead. It is expected that ongoing emission analysis concerning fatty acids will confirm these observations.

INTRODUCTION

The current study focuses on the emissions behaviour of wood and the corrosion of metals due to these emissions. In contrast to the test results of former and current studies, it is assumed that both materials are highly compatible. However, interactions between certain metals and wood can occur through direct contact of metal fittings with wood or indirectly through the environment when metal objects are transported, stored, or displayed in wooden cases. Wood can be considered to be one of the major sources of formaldehyde (FA) emissions and other volatile compounds. An initial molecular layer of water on a metal surface can start forming at a relative humidity of 20%, and this reacts with atmospheric formaldehyde to produce formic acid which in turn causes metal corrosion (Hatchfield *et al.* 1986). An increased wood moisture content combined with higher temperature augments the formation of acetic acid. The purpose of this study was to develop and test a suitable method for minimizing emissions from bio-based products, in particular wood. In contrast to the emissions derived from urea-formaldehyde resin, FA emissions from untreated wood have been considered to be insignificant (Meyer and Boehme 1997). In spite of these observations, Schäfer and Roffael (2000) proposed reaction mechanisms for FA formation in wood and demonstrated an increase in FA emissions at elevated temperatures and prolonged heating times during panel production. In particular, during the pressing step at elevated temperatures, an increase in FA and VOC emissions were detected in the absence of any resin (Carlson *et al.* 1995). Even at temperatures below 100°C, as is the case during the kiln drying of wood, the hydrolysis of cell wall components (cellulose, polyose/hemicellulose and lignin) leads to the formation of furfural, formaldehyde and very volatile acids (e.g. formic acid, which is a very volatile organic compound). The approach following these studies was to reduce emissions from solid wood products through a combination of impregnating the wood with a phosphate-buffer-solution and the smooth thermal treatment of the wood below a critical temperature of 40 °C, at which point the formation of formaldehyde increases. The aim of this study was to develop low emission wood, which is suitable as a building product in sensitive environments.

MATERIALS AND METHODS

The selected test set up consisted of wood species known to have low emissions such as alder, and wood species with emission rates that were expected to be higher such as ash and oak. Six samples of each species were impregnated with a buffer-solution and were dried under vacuum conditions to an absolute dry state along with a further six untreated samples. A pH range of 3.3 to 7.2 for hardwoods (e.g. 5.5 for alder and 3.3 to 3.9 for oak) has been found (Cole 1979). The impregnation with the buffer solution (pH = 7.2) was performed in a laboratory-scale impregnation plant. All pH measurements were made with a WTW pH meter, Model inoLab according to the technique described by Lambuth (1967). In this study, measurement of the emissions from wood were performed on the basis of ISO 16000-10 (2006) with a microchamber. The specimens were installed under constant conditions with respect to temperature, relative humidity and air exchange rates (Figure 1).

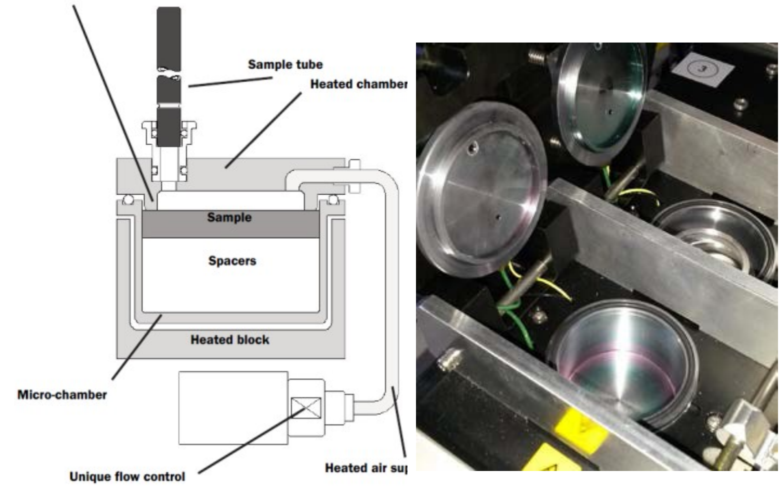

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Figure 1: (left) Laboratory Microchamber- Schematic, (right) Laboratory Microchamber

The samples were prepared according to EN ISO 16000-11, formatted (Ø 40 mm) and stored in a conditioning room (23 ± 2 °C and 50 ± 5 %). Prior to the tests, fresh surfaces were planed. The stainless steel cell allowed a controlled climate of 23 ± 1 °C and 50 ± 3 % RH. The inlet air flow was set to 40 mL/min for a duration of 1200 minutes to collect VOCs using Tenax® adsorbent tubes (containing 200mg of Tenax® polymer). Aldehydes were collected with the same air flow, but only for a duration of 300 minutes using 2,4- DNHPH adsorption cartridges. The Tenax® samples were desorbed (UltrA/ Unity^2, Markes Inc.) and detection was carried out using GC/ FID Clarus 480, GC MS Clarus 680 PerkinElmer and NIST library spectra. The emission rate of volatile compounds in the outlet air was calculated as shown in equation 1 (Eqn.1).

Emission rate (ug/hr)
= sample concentr. (ug/ml) * sample volume (ml) / time of sorption (hrs)) (1)

Low aldehydes were identified by high-performance liquid chromatography (HPLC; EN ISO 16000-3). The DNPH cartridges were extracted with acetonitrile and analysed via HPLC using a variable wavelength detector (Varian ProStar, Crawford Scientific). In addition several field trials and laboratory exposure were performed to investigate the corrosive characteristics of the gases. Using the Oddy test (Oddy 1973), potential damage to art objects through formaldehyde and organic acid (formic and acetic) vapour can be accelerated by the addition of a small amount of water (1 ml), elevation of temperature to 60 °C and storage for 28 days; this prompts the evolution of potentially corrosive gases from the test material and metal corrosion reactions.

RESULTS AND DISCUSSION

Impregnation with the buffer solution led to the effect intended. The results showed that the buffer system with a pH value of 7.2 caused an increase in the pH values of the three different species: alder (6.22 to 6.65), oak (4.72 to 5.27) and ash (5.82 to 6.82). Subsequent investigations carried out to determine emissions and the degree of corrosiveness were affected by the decreased acidity of the specimens. Emissions from the untreated and treated samples of the different species were compared (Figure 2)

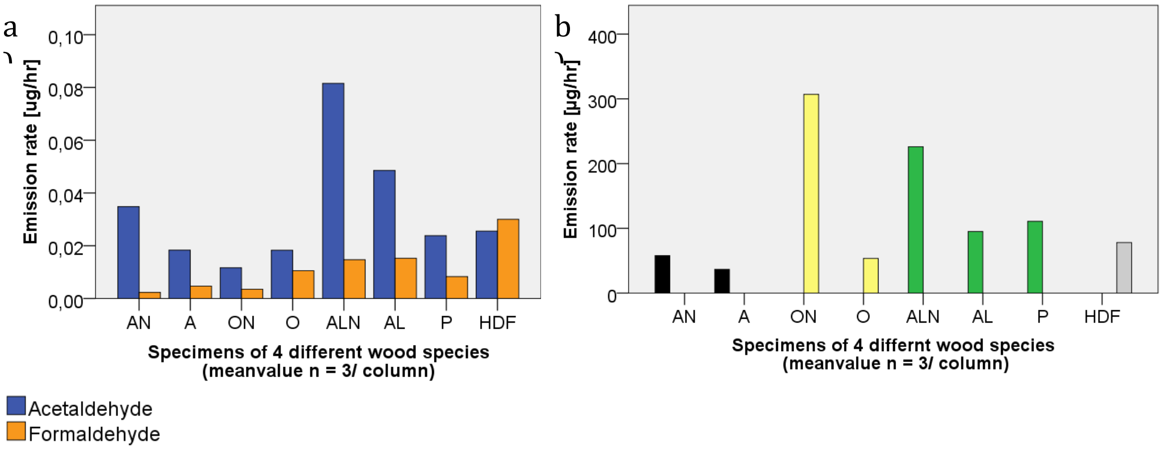

Figure 2: a) Emission rate (µg/hr) of Acet- and Formaldehyde (mean-values of 3 samples): AN = Ash untreated, A = Ash impreg., ON = Oak untreated, O = Oak impreg., ALN = Alder untreated, AL = Alder impreg., P = Alder Plasma treated, HDF = (Beech/ Pine) High Density Fiber Board
b) Sum of emissions of aldehydes having C>2 (i.e. furfural, hexanal, heptanal, octanal, nonanal and decanal)

Small amounts of low aldehydes, i.e. formaldehyde (FA) and acetaldehyde (AA), were detected in the untreated and impregnated specimens of all species, conditioned at 20 °C and RH of 65 % ahead of the emission tests. In contrast to the untreated specimens (AN, ALN), the additional impregnation of the ash and alder (A, AL) samples gave even lower emission rates. These results imply that the buffer treatment led to a reduction in emissions. Concerning this analysis, it needs to be taken into account that these differences were measured only on a very small scale. The investigations showed that additional plasma-treatment (P) of the impregnated alder samples decreased the emissions even more. HDF samples were examined as references in order to confirm the applied test method. The amount of aldehydes determined, having C>2 (sum of furfural, hexa-, hepta-, octa-, nona-and decanal), were summed up as VOCs for the impregnated and untreated samples. As shown in Figure 2b the VOCs from the native specimens were far greater than those of the treated samples. The results indicate the positive influence of the buffer treatment on the chemical compounds. However, acet-, formaldehyde and VOCs possess very little corrosiveness towards materials like textiles, paper and metals. In contrast, the vapours of organic acids (formic and acetic acid) are known to be reactants in metal corrosion. This became visible during the Oddy tests when lead coupons were removed from the test vessels. Due to the increased amounts of water available in the vessel, the results became more pronounced, to the point of being rated as unsuitable because of the heavy corrosion.

CONCLUSIONS

The study considered direct emissions as well as secondary products, relating to the formation of acids and aldehydes caused by thermo-hydrolysis during processing and testing. It was found that the laboratory micro-chamber was an appropriate for of instrumentation for the performance of experiments to investigate the emission rate from small-sized samples. The GC/FID, MS and HPLC analyses were essential for the investigations. Impregnation with a phosphate-buffer-solution and vacuum drying resulted in a lower sample FA/AA content. As a result of advanced treatments, especially plasma treatment, the formation of formaldehyde and VOCs was supressed, achieving the goal of enhanced bio-based building products for sensitive environments such as health care institutions or museums.

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Fast PEG-Based Oak-Wood Treatment for Reduced Swelling Behaviour

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Keywords: anti-shrinkage efficiency (ASE), impregnation, oak wood, polyethylene glycol (PEG), silane

ABSTRACT

The good dimensional stabilising properties of polyethylene glycol (PEG) impregnated in wood are well described and investigated. The common method to impregnate wood with PEG is to store the samples for several weeks in the PEG-solution and let the PEG diffuse into the wood. This method is used to stabilize archaeological wood, but it is not suitable for industrial application. Therefore a short-term vacuum-pressure cycle was used to impregnate oak with different PEG-solutions. Using the same procedure, oak-wood was also impregnated with PEG-functional silane, which provides nearly the same benefits as PEG, but it does not leach out in an aqueous environment like PEG does. The PEG impregnation resulted in weight-percent-gain-values (WPG) of up to 42 %, which is comparable with the common impregnation method by diffusion only. A radial anti-shrinkage-efficiency (ASE) of more than 70 % was found. Modification with PEG-functional silane showed a WPG of 32 % and a comparable ASE to PEG impregnation. These results show the potential for the use of PEG (-functional) wood treatment in more critical climate conditions or even in outdoor use.

INTRODUCTION

The good dimensional stabilising properties of PEG impregnated into wood are well described and investigated. The common method of impregnating wood with PEG, is to store the samples for several weeks in the PEG-solution and let the PEG diffuse into the wood. This method is used to stabilize archaeological wood, but it is not suitable for industrial application since it needs a very long time to achieve sufficient WPG values. Vacuum-pressure impregnation is a common method in wood modification to treat wood with modification agents. In this study such a method was applied on oak wood impregnated with PEG. Schneider (1969) carried out extensive research on the PEG treatment of pine and beech wood. He found good dimensional stabilisation of up to 90 %. Higher values were possible, but with higher WPG and moisture contents, the wood became “moist” on the surface. Bjurhager *et al.* (2010) did some research on the mechanical properties of small specimens of PEG impregnated oak wood. They found only a slight reduction in the axial tensile modulus and strength, but detected up to 50 % lower compressive modulus and yield strength in the radial direction. They explained this observation by the altered microfibril angle, effected by the swelling of the specimens. To find a PEG impregnation that is suitable for critical climate conditions, PEG 400, PEG 1000 and PEG-functional silane was impregnated in a short-term vacuum-pressure treatment cycle to investigate ASE and leaching behaviour under different climate conditions.

MATERIAL AND METHODS

One hundred oak wood specimens (*Quercus* spp.) were cut with dimensions of 25x24x10 mm³ (rad./ tang./ long.). All specimens were dried at 103°C to determine dry mass. Groups of 10 pieces were formed and were treated according to Table 1. Polyethylene glycol (PEG) 400 and PEG 1000 have an average chain length of 400 and 1000, respectively, the silane used has on the one hand PEG functionality and on the other hand methoxy functionality.

The specimens in each group were impregnated in an impregnation solution of 150 ml. The reference specimens were impregnated with water to provide a comparable wetting and drying treatment. The impregnation cycle was performed in an autoclave. In the first step the pressure was reduced to 15 kPa for 30 min. In the second step the pressure was raised to 800 kPa for 12 h. Finally, atmospheric pressure of 1 bar was again established. The specimens were dried again at 103°C to determine the WPG.

Table 1: Impregnation parameters and WPG

Group	Treatment agent	Concentration in water [%]	Solution uptake [%]	Weight percent gain (WPG) [%]
1	Reference	-	100.24	-3.17
2	PEG 400	15	99.76	10.60
3	PEG 400	30	101.04	24.94
4	PEG 400	45	104.90	42.26
5	PEG 1000	15	98.82	10.24
6	PEG 1000	30	99.82	24.06
7	PEG 1000	45	98.63	40.80
8	Silane	15	100.29	11.17
9	Silane	30	100.43	22.41
10	Silane	45	94.01	31.88

To investigate the anti-shrinkage efficiency (ASE) a series of changing climatic conditions were used. Full water saturation was avoided because PEG would leach out again. Before and after each condition the specimens were dried at 103°C to determine the dry mass. The climates investigated are shown in Table 2. The time in each condition was 10 days.

Table 2: Tested climate conditions

Climate cycle no.	Temperature [°C]	Relative humidity [%]
1	30	70
2	20	95
3	20	90
4	20	90

Table 3: Results climate cycles: WPG, moisture content and radial ASE

				1st cycle 30°C / 70%relH.			**2nd** cycle 20°C / 95%relH.			**3rd** cycle 20°C / 90%relH.			**4th** cycle 20°C / 90%relH.		
Group	**Treatment**		**initial WPG**	**WPG**	**Moist. cont. [%]**	**ASE (rad)**	**WPG**	**Moist. cont. [%]**	**ASE (rad)**	**WPG**	**Moist. cont. [%]**	**ASE (rad)**	**WPG**	**Moist. cont. [%]**	**ASE (rad)**
1	Reference		-3.17	-2.79	11.40	-	-3.28	20.19	-	-2.59	16.40	-	-3.42	14.50	-
2	PEG 400	15%	10.60	10.49	11.82	14.19	10.17	27.37	39.79	10.22	19.19	36.98	10.00	18.90	34.50
3	PEG 400	30%	24.94	24.80	13.55	41.78	23.87	37.86	71.68	23.80	25.03	46.04	23.42	24.71	44.79
4	PEG 400	45%	42.26	41.96	16.53	65.32	31.55	43.95	75.79	31.48	29.10	40.12	30.66	28.17	31.89
5	PEG 1000	15%	10.24	10.29	11.52	8.32	10.09	25.30	31.74	10.17	18.44	28.12	9.90	17.90	25.08
6	PEG 1000	30%	24.06	24.05	12.47	23.92	23.75	34.17	59.16	23.90	23.30	48.17	23.51	22.38	42.75
7	PEG 1000	45%	40.80	40.79	14.60	46.69	33.31	39.70	74.61	33.48	27.15	53.51	33.01	26.17	48.01
8	Silane	15%	11.17	11.36	10.87	10.55	10.80	23.47	15.56	11.23	17.39	18.21	10.61	16.04	15.06
9	Silane	30%	22.41	22.44	10.94	22.42	21.85	28.15	32.94	22.05	19.51	27.63	21.49	18.30	24.44
10	Silane	45%	31.88	31.72	11.12	28.81	31.02	31.38	41.57	31.12	21.25	28.58	30.56	19.95	30.33

RESULTS AND DISCUSSION

The results of the WPG and ASE measurements confirm, in principle, the suitability of a short-term vacuum-pressure impregnation method for PEG and PEG-functional silane. The loading with impregnation agents are comparable to the literature and provide a certain ASE. Bjurhager et al. (2010) impregnated oak wood samples with PEG 600 using a long-term, pressure-less method and achieved lower, but comparable, WPG values. There is a strong positive correlation between the impregnation agent concentration and the resulting WPG value (Figure 1). Schneider (1969) also found a similar connection for PEG impregnated pine wood.

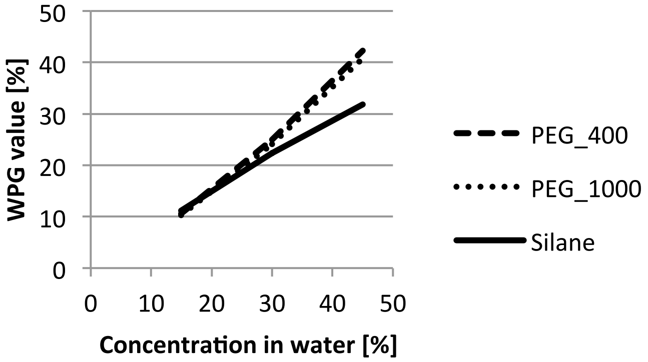

Figure 1: Correlation between treatment agent concentration and WPG value

The ASE values, normally investigated on water saturated specimens, were determined in this study using different climate conditions. Radial ASE increased with rising wood moisture contents. But also the wood moisture content increased with higher WPG (Figure 2) due to the hygroscopic properties of PEG (Schneider 1969; Bjurhager *et al.* 2010). Even though no classical leaching test or storage under water was performed, leaching was observed in the second climate cycle in the highly loaded PEG 400 and PEG 1000 specimens. Here, the wood moisture content exceeded a certain value, leading to leaching of the treatment agent (Figure 3). That effect was also found by Schneider (1969).

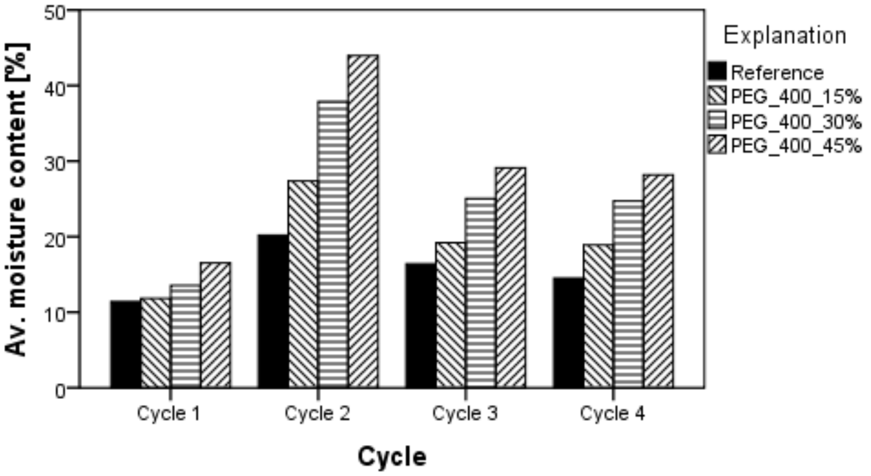

Figure 2: Moisture content in each climate cycle for PEG 400 and reference specimens

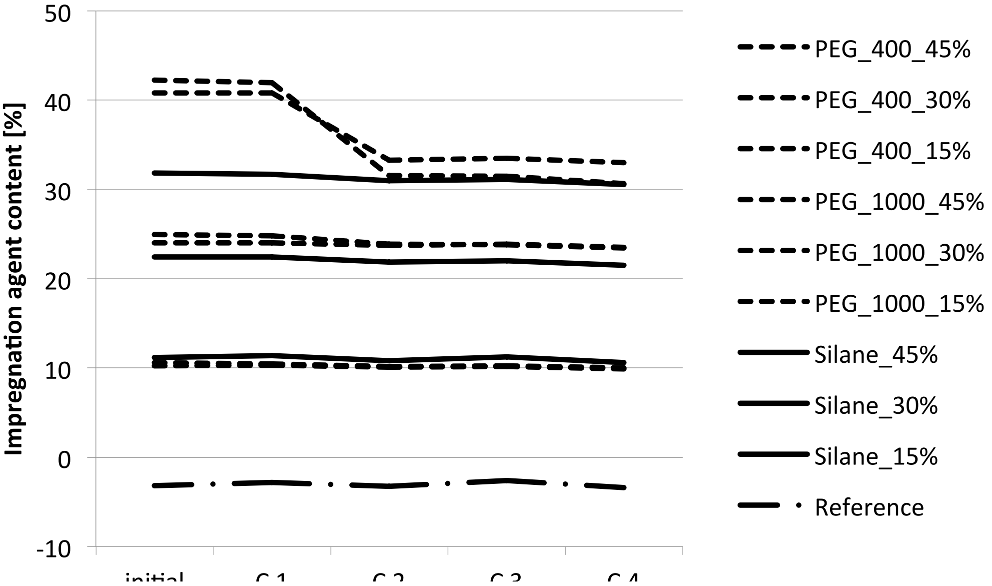

Figure 3: Change in WPG values after 4 cycles. In the second cycle the WPG values for the heavy loaded PEG 400 and PEG 1000 groups decrease because of leaching effects in the high humid climate.

The results show the potential for using PEG and PEG-functional silane treated oak wood in areas with moderate climatic conditions. The WPG and ASE needed can be easily controlled by the concentration of the impregnation solution. Testing the suitability of PEG-functional silane modified oak or outdoor use wood is part of current investigations.

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Hydrophobation of Timber with Organosilicon Compounds – An Update from the SILEX Life+ Project

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Keywords: organosilicon compounds, silicones, treatment, water repellence, hydrophobation

ABSTRACT

The SILEX project, “Improving sustainability of construction materials using innovative Silicon based treatment”, is a Life+ project with the reference LIFE+11 ENV/BE/1046 and runs from April 2013 up to end of August 2016. This project intends to demonstrate that a new class of compounds can be used for wood treatment for extended durability and that the testing phase could be accelerated according to a new testing methodology. The project aims to demonstrate that treatments with silicon-based hydrophobers have a lower impact on the environment with a lower need of biocide use than the current techniques. This project update intends to present some preliminary results showing potential to use this technology.

INTRODUCTION

The overall objective of this project is to extend the lifetime of constructions made of wood materials by providing water repellent properties to the materials thanks to “Si-based” solutions. Several studies have already explored the use of silane or siloxane as a hydrophober for wood (De Vetter *et al.* 2010, Mai and Militz 2004, Ghosh *et al.* 2009, 2012).

Wood is subject to water infiltration in both liquid and vapour phases. As the moisture content increases, wood will swell until it reaches its maximum dimension at its fibre-saturation point (about 30% moisture). Rapid dimensional changes resulting from changes in the level of bound water cause the wood to crack and split. These cracks will then allow moisture to absorb easily and quickly into the wood. At some moisture content levels and depending on the time of wetness, moisture will be present as free water, which in turn promotes the rate of wood decay.

This update of the project intends to present some preliminary results showing potential to use this technology.

Various silicon-based hydrophobers (non-film forming) were screened and tested as “impregnation hydrophobers” on three European wood species (pine, beech, oak). Different application methods were used as well (vacuum impregnation, brushing, dipping). The first results demonstrate that treatments with selected organosilicon compounds enable the minimization of water absorption in wood without affecting the rate of water desorption or hardness. As an example three commercial water repellents, differing by not only the active material but also the delivery system were used side by side to treat wood specimens by vacuum impregnation.

EXPERIMENTAL

A water soluble silane (SIL A), an emulsion of a mix of siloxane/silane/resin (EM A) and a microencapsulated siloxane polymer (MIC A) were used for vacuum impregnation.
Table 1 gives the Weight Percent Gain (WPG) measured after vacuum impregnation. Despite the very different type of delivery system, no large differences of WPG, for the different wood species and water repellents are observed.

Table 1: weight percent gain after vacuum impregnation of wood specimens with different water repellents

	EM A	**MIC A**	**SIL A**
WPG	(%)	(%)	(%)
Pine	1,1	1,13	1,17
beech	1,09	1,5	0,97
oak	0,43	0,46	0,4

The wood pieces were weighed and placed on metallic supports such that a small surface area was in contact with water (Figure 1). The immersed part of the wood pieces was adjusted to remain at 2 mm during the entire test period (72 hours of contact time with water). The wood specimens were placed in contact with water for 72 hours and then left to dry for the rest of the duration of the experiment.
Water uptake was calculated to study the absorption and desorption rate of the treated wood. Samples were put in contact with water to measure “longitudinal” water absorption. Wood specimens were removed, towelled and weighed at regular time interval.

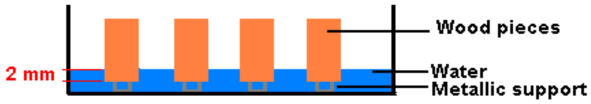

Figure 1: experimental set up to measure “longitudinal water absorption”

The rate of drying was assessed by removing the wood specimens from water after 72 hours, placing them on grids in the lab and further weighing them as a function of time until they reached constant weight.
Water uptake given in this paper was measured using capillarity absorption along the longitudinal axe. Only “longitudinal” water absorption was measured and reported in this study, as this measurement enables easy differentiation between different water repellents for wood.

RESULTS AND DISCUSSION

The following graphs (Figure 2) show the weight gain (averaged value of three individual measurements) due to the water uptake (as % of the initial dry weight) plotted as a function of contact time with water or drying time.

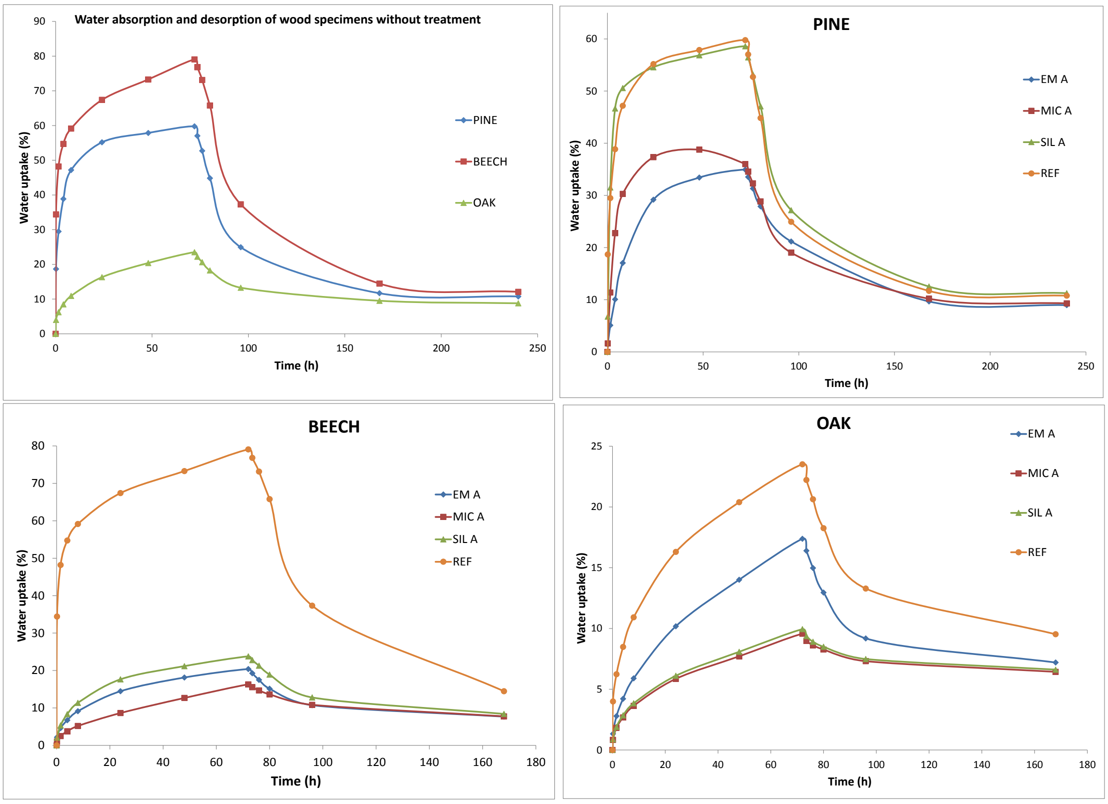

Figure 2: water uptake (as a % of initial wood specimen dry weight) as a function of contact time with water and after 72h, as a function of drying time

It is clear that the use of different silicon-based water repellents reduce water penetration to different extents with the different wood species. It can be observed that the treatment of wood specimens with silicon-based water repellents does not slow down rate of drying, which was expected, since they are not film forming.

The treated wood was also subjected to many other different tests as well. The results indicate, for example, that fungal growth and termite feeding behaviour is affected by treatment with some water repellents. Establishing the relationship between mechanical properties, resistance to fungi or fire resistance with the water uptake of the impregnated wood was initiated.

A straightforward absorption-desorption lab test as well as a high-end neutron approach enabled a detailed investigation of the moisture dynamics of modified wood and in that way the efficacy of treatment (Li *et al.* 2014).

A study on the impact of impregnation of wood specimens with a silicon-based hydrophober on extractable leaching was also initiated.

ACKNOWLEDGEMENTS

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Mould Resistance, Dimensional Stability and Colour Stability of Scots Pine Modified with Organo-Silanes Alone, and in Combination with BAC Fungicide and/or Acrylic Coating

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Keywords: acrylic-paint, colour, fungicides, organo-silanes, moulds, pine, swelling

ABSTRACT

This work deals with the modification of Scots pine (*Pinus sylvestris*) sapwood with four organo-silanes (MTMS – methyltrimethoxysilane; VTMS – vinyltrimethoxysilane; PTMS – propyltrimethoxysilane; or APTMS – 3-aminopropyltrimethoxysilane), applied in 10% water solutions, in terms of their effect on its mould resistance, dimensional stability and colour stability. The pine specimens were modified by dipping with organo-silanes alone, or in a mixture with 2% BAC fungicide. Finally, selected groups of modified specimens were painted with the transparent acrylic coating Balakryl-Dixol. The growth activity of the moulds *Aspergillus niger* and *Penicillium brevicompactum* was inhibited only by the 3-aminopropyltrimethoxysilane (APTMS), while other organo-silanes had no anti-mould efficiency – not even in combination with the final coating. The BAC used in mixtures with individual organo-silanes suppressed activity of the *P. brevicompactum*, but this fungicide was not effective against the *A. niger*. The anti-swelling efficiency (ASE) of the pine specimens modified with organo-silanes was in the range from 16 to 18%, or for the APTMS up to 34%. The three organo-silanes without $–NH_2$ group changed the initial colour of the pine sapwood only a little, and the total colour difference ΔE^* was not greater than 2. Only the APTMS caused an apparent yellowing of the specimens with an increase in the ΔE^* close to 10. One-week exposure of modified specimens in a Q-SUN Xe-1-S Xenotest caused their darkening, yellowing and reddening, and the final transparent acrylic coating suppressed these colour changes *ca*. about 30%.

INTRODUCTION

3. Organo-silanes are monomeric molecules with four organic groups (*e.g.,* one alkyl and three alkoxy) covalent bonded to the silicone atom. The presence of these molecules in modified wood improve its water and weathering resistance (De Vetter *et al.* 2010), and some organo-silanes (*e.g.,* if $–NH_2$ functional group is bound to an organic group) can also inhibit decay, mould and other biodeterioration processes in the lignin-polysaccharide matrix of wood cells (Donath *et al.* 2006, Reinprecht and Grznárik 2014). Organo-silane molecules themselves are not stable in wood and, therefore, firstly have to react with molecules of water creating silanoles, which in turn can react with – the OH groups of wood, thereby reducing its hygroscopic character (Hill 2006).

4.

EXPERIMENTAL

Wood

Specimens were prepared from the sapwood of healthy Scots pine (*Pinus sylvestris* L.) boards without knots or other growth inhomogeneity. The specimens were 50x10x5 mm (LxRxT) for the mould resistance tests, and 25x25x3 mm (LxRxT) for the swelling and colour tests.

Modification agents – organo-silanes and BAC fungicide

In the experiment, all four organo-silanes, the MTMS (methyltrimethoxysilane), VTMS (vinyltrimethoxysilane), PTMS (propyltrimethoxysilane) and APTMS (3-aminopropyltrimethoxysilane), provided from Sigma-Aldrich Chemie Steinheim – Germany, were applied in 10% (m/m) aqueous solutions: (1) alone, or (2) with the addition of 2% (m/m) of the BAC (benzalkonium chloride) fungicide from the Bochemie Bohumin – Czech Republic.

Modification of wood and painting of wood surfaces

Specimens with an equilibrium moisture content (EMC) of *app.* 8% were modified by dipping at a temperature of 20°C for 3 minutes. Their subsequent drying at 60°C for 6h and conditioning again to an EMC of *app.* 8% was performed in accordance with Reinprecht and Grznárik (2014). The transparent acrylic coating, Balakryl-Dixol (Trilak festékgyártó Kft. Budapest – Hungary), was painted on selected groups of specimens at a rate of 2 x 100 g/m^2.

Accelerated weathering in Xenotest

Accelerated weathering of the modified specimens, in a Q-SUN Xe-1-S Xenotest (Q-Lab Corporation, USA), was performed with the aim of testing their colour stability. A one-week long exposure cycle according to a partly modified EN 927-6 (2006) consisted of: 1st Step → 24 h at 45 ± 3°C; 2nd Step → 48 sub-cycles each lasting 3 h (2.5 h = UV irradiance 0.55 W/m^2 from 1800 W xenon lamp at 340 nm; and 0.5 h = water spray at 20 ± 1°C).

Growth activity of moulds

The growth activity of the moulds (GAM from 0 to 4; 0 is no growth, 1 is growth on ≤ 10% of specimens; 2 is ≤ 25%; 3 is ≤ 50%; 4 is > 50%), *Aspergillus niger* Tiegh. and *Penicillium brevicompactum* Dierckx, on the top surfaces of the modified and reference specimens was tested over 28 days at 28 ± 2°C according to the standard STN 49 0604 (1980).

Volume swelling and anti-swelling efficiency

Values of the volume swelling (β_V) of the modified and reference specimens were used for the determination of the anti-swelling-efficiency (ASE) of individual organo-silanes.

Colour and its stability at weathering

The colour coordinates of the natural, modified and weathered specimens in the CIE-$L^*a^*b^*$ system were analysed in their centre with the Color Reader CR-10 (Konica Minolta, Japan). The total colour differences ΔE^* were computed by CIE (1986), arising from changes in ΔL^* (white – black), Δa^* (red – green), and Δb^* (yellow – blue) between the final (a/ modified; b/ weathered) and initial (a/ reference unmodified; b/ modified) states (Eqn. 1):

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

RESULTS AND DISCUSSION

Mould resistance

From the organo-silanes tested, only the 3-aminopropyltrimethoxysilane (APTMS) partly suppressed the growth activity of *Aspergillus niger* (Table 1), and significantly suppressed the growth activity of *Penicillium brevicompactum* (Table 2). Gosh *et al.* (2009) also determined an increase in the anti-mould resistance of wood modified with a macro-emulsion of amino-silicones which, like APTMS, also contain a $–NH_2$ group.
The other organo-silanes tested did not have any anti-mould efficiency, either with or without the presence of the final transparent acrylic coating (Table 1, Table 2).
BAC together with organo-silanes suppressed activity of the *P. brevicompactum* (Table 2). On the other hand, this fungicide was not effective against *A. niger* (Table 1).

Table 1: The growth activity of mould (GAM) Aspergillus niger (0-4) on the pine sapwood modified with 10% organo-silanes alone, or in combination with 2% BAC and/or acrylic coating

Modification system	MTMS	VTMS	PTMS	APTMS
Organo-silane alone	4	4	4	3.5
Organo-silane + coating	4	4	4	2
Organo-silane and BAC	3.5	3.5	3.5	1.5
Organo-silane and BAC + coating	3.5	3.5	3.5	1.5

The GAM for the reference was 4. Mean values are from 4 specimens. (Notes are also valid for Table 2).

Table 2: The growth activity of mould (GAM) Penicillium brevicompactum (0-4) on the pine sapwood modified with 10% organo-silanes alone, or in combination with 2% BAC and/or acrylic coating

Modification system	MTMS	VTMS	PTMS	APTMS
Organo-silane alone	4	4	4	2
Organo-silane + coating	4	4	4	0
Organo-silane and BAC	2	0	0	0
Organo-silane and BAC + coating	1	0	0	0

Dimensional stability

The volume swelling of the pine sapwood specimens (having an initial EMC of *app.* 8%) in distilled water was decreased from 10.8% to 8.9 – 9.1% due to presence of the MTMS, VTMS, or PTMS, and even to 7.1% due to the presence of the APTMS (Table 3).
The ASE of the APTMS treated material was *app.* twice as high (ASE = 34.3 %) as the other organo-silanes (ASE = *ca.* 16 – 18%). The significant increase in the dimensional stability of the pine sapwood modified with the APTMS can be explained by the creation of strong interactions between the $–NH_2$ groups of this organo-silane and the –OH groups in lignin-polysaccharide matrix of wood. A high ASE (*ca.* 30 %) was also determined by Donath *et al.* (2004) for beech wood treated with TEOS (tetraethoxysilane), MTES (metyltriethoxysilane) and PTES (propyltriethoxysilane) treatment; *i.e.,* ASE depends on the WPG, as well.

Table 3: The volume swelling of modified pine sapwood ($\beta_{v\text{-}mod}$) after 24 h of soaking in water, and the anti-swelling efficiency (ASE) and weight-percent-gain (WPG) of organo-silanes (C = 10%)

Tested parameter	MTMS	VTMS	PTMS	APTMS
$\beta_{v\text{-}mod}$ [%]	8.9 (1.6)	9.0 (1.1)	9.1 (1.2)	7.1 (0.4)
ASE [%]	17.6	16.7	15.7	34.3
WPG [%]	3.4 (0.6)	3.6 (0.6)	3.2 (0.8)	3.1 (0.7)

The β_v of the reference unmodified pine was 10.8% (determined from its EMC app. 8% to moisture above FSP). Mean values are from 6 specimens. Standard deviations are in parentheses.

Colour stability

Organo-silanes without the –NH_2 group (MTMS, VTMS, and PTMS) only changed the colour coordinates of the modified pine sapwood slightly, either with or without subsequent painting with a transparent coating, *i.e.*, the $\Delta L^{\cdot}$ was from 0.7 to -0.8, $\Delta a^{\cdot}$ from 0.6 to -0.4, $\Delta b^{\cdot}$ from 0.8 to -0.4, and $\Delta E^{\cdot}$ from 0.8 to 1.6. On the other hand, the APTMS (with –NH_2 group) had an evident effect on the colour of pine sapwood: $\Delta L^{\cdot}$ was -4.3 or -4.9, $\Delta a^{\cdot}$ 2.2 or 3.0, Δb 7.2 or 7.9, and $\Delta E^{\cdot}$ 8.8 or 9.9.

The colour stability of modified pine sapwood during ageing in the Xenotest was comparable with the reference one. Due to the acrylic coating it increased by about 30% (Table 4).

Table 4: The colour change in CIE-L·a·b· of modified pine sapwood after 1-week exposure in Xenotest

Modification system	Colour parameter	MTMS	VTMS	PTMS	APTMS
Organo-silane alone	$\Delta L^{\cdot}$	-11.4	-10.3	-9.2	-10.8
	$\Delta a^{\cdot}$	6.4	5.7	5.2	5.0
	$\Delta b^{\cdot}$	7.0	7.9	6.3	3.2
	$\Delta E^{\cdot}$	14.9	14.4	12.4	12.5
Organo-silane + coating	$\Delta L^{\cdot}$	-8.1	-6.6	-7.3	-6.1
	$\Delta a^{\cdot}$	6.5	4.8	5.8	2.6
	$\Delta b^{\cdot}$	4.6	3.7	3.5	-1.7
	$\Delta E^{\cdot}$	11.5	9.2	10.2	7.4

The colour changes of the reference pine: $\Delta L^{\cdot} = -10.3$ (1.5), $\Delta a^{\cdot} = 6.2$ (0.8), $\Delta b^{\cdot} = 7.4$ (2.4), $\Delta E^{\cdot} = 14.2$ (2.4). Mean values are from 6 specimens. Standard deviations for the reference pine are in parentheses.

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Standards: EN 927-6 (2006); STN 49 0604 (1980), STN 49 0126 (1988), CIE (1986).

Effect of Phenol-Formaldehyde (PF) Resins Oligomer Size to the Dimensional Stability of Treated Beech Wood

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Keywords: average molecular weight, beech, form stability, phenol-formaldehyde resin

ABSTRACT

The objective of this study was to examine the impact of phenol-formaldehyde (PF) resins on the dimensional stability of European beech wood (*Fagus sylvatica*). Four different resins (A, A1, B and B1) were used as impregnation agents. Wood blocks of 25x25x10 mm^3 were vacuum impregnated with the water soluble resin, where the concentration of impregnation agent was 9, 18 and 27 wt % in water. The anti-swelling efficiency (ASE) of the untreated and treated samples during seven soaking and drying cycles was evaluated. With regard to the dimensional stability of wood, the results showed that the ASE of the treated wood was in the range from 51 to 66%, despite an equal resin loading in wood. The ASE of wood treated with resins A and A1 was up to 25% greater than those treated with resin B1. 30 to 35% and 15 to 20% greater bulking was achieved for wood specimens treated with resins A and A1 compared to resins B and B1, which clearly confirm the importance of the molecular size of the PF resin.

INTRODUCTION

Recently, researchers worldwide have tried to develop new technologies to modify wood to improve some of its properties such as dimensional stability, UV/sunlight resistance and biological durability. A comprehensive overview of existing wood modification techniques and protection mechanisms is given by Hill (2006). One of the promising techniques involves the use of synthetic resins such as N-methylol resins, phenol-, urea- and melamine-formaldehyde resins.

Usually thermosetting resins are used as a binder in wood composite products, such as plywood, oriented strand board (OSB), laminated veneer lumber (LVL) and fiberboard. PF resins are also used for wood and wood product modification. The treatment of wood with water soluble PF resin is a well known and effective method to improve the dimensional stability.

A lot of research has been done to assess the dimensional stability of wood and wood products due to the different average molecular weights (M_w) of PF resins (see table 1). Hence, high dimensional stability in wood can be achieved in two ways: via high loading of resin into wood or by additional treatment (compression). Up to now, there has been no systematic investigation related to the average molecular size of PF resin and its influence on the anti-swelling efficiency of hardwoods. Therefore, the aim of this study was to evaluate the impact of different molecular sizes of PF resin oligomers on the dimensional stability of beech wood.

Table 1: Overview on dimensional stability of wood and wood products due to different average molecular weight (M_w) of PF resins

Wood	M_w [g/mol]	WPG [%]	Bulking [%]	ASE [%]	Reference
Japanese cedar (*Cryptomeria japonica*)	290	46	12.6	65	Fununo *et al.* 2004
	309	30	-	60	
	335	30	-	60	
	470	19	3.2	26	
	820	42	-	-	
	1078	30	-	12	
Scots pine (*Pinus sylvestris*)	400	35-50	11-14	-	Klüppel and Mai 2013
Compressed Hybrid poplar Cross (*Populus deltoids and trichocarpa*)	172	16.5	-	86	Gabrielli and Kamke 2010
	780	23	-	66.5	
White pine (*Pinus strobes*)	-	77	-	37	Stamm and Seborg 1936
Redwood (*Sequoia sempervirens*)		47.5		40	
Red maple (*Acer rubrum*)		42.7		60.2	

EXPERIMENTAL

Wood

To assess the impact of resin on the dimensional stability of European beech (*Fagus sylvatica*) wood, specimens with dimensions of 25x25x10 mm^3 (*r x t x l*) were prepared. The oven dry weights were determined after drying at 103±2°C for 24 hours. After drying the specimens were impregnated (using vacuum) on the same day. Ten replicates per group were used.

Phenol-formaldehyde resins

Before being used for impregnation the stock solutions of different types of PF resins were diluted to 9%, 18% and 27% (w/w). As listed in table 2, four types of resin were used to prepare the aqueous solutions.

Table 2: Characteristic parameters of PF resin compositions used in the study

Resin	M_w [g/mol]	Solid content [%]	Catalyst	Amount of formaldehyde [%]	Free phenol [%]
A	297	49.5	NaOH	<1	<4
A1	421	49.0	NaOH	<1	<4
B	655	58.4	NaOH	<1	<4
B1	854	47.8	NaOH	1.88	0.24

The treatment of wood, as well all calculations related to anti-swelling efficiency (ASE) are described in Biziks *et al.* (2015a, 2015b)

RESULTS AND DISCUSSION

Dimensional stability was assessed on beech wood treated with different PF resins. In order to find out correlation between ASE and penetration depth and loading of resin into beech wood tissue, a series of impregnations were also carried out. Figure 1 clearly shows the positive effect of treatment with PF resin on the dimensional stability of beech wood and remains comparatively constant during cyclic tests. Regardless of the resin used for treatment, the long-term dimensional stability was not influenced. This might be explained by good fixation of the PF into the wood tissue and resistance to hydrolytic conditions, resulting from sufficiently deep deposition into, and the development of a highly cross-linked 3D network in, the wood cell walls, without an in-depth alteration of the cell wall chemistry. However, different magnitudes of ASE values were achieved. Specimens treated with resins A and A1 achieved approximately 20-25% higher ASE values compared to specimens treated with resins B and B1. Both wood sample groups treated with resins A and A1 exhibited highest ASE values of 66% compared with that of wood blocks treated with resins B and B1 of 56 and 51%, respectively.

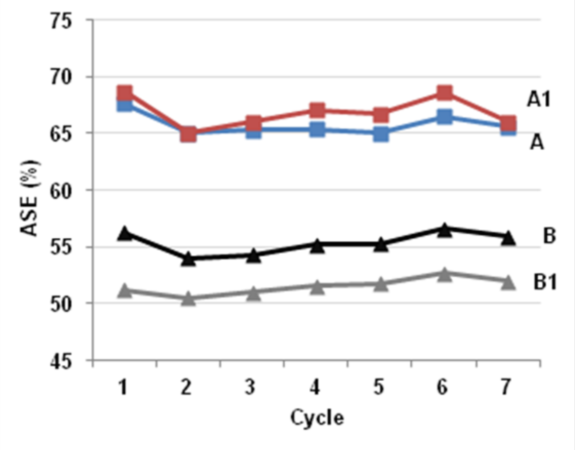

Figure 1: Dimensional stability of beech wood during 7 cycles of water saturation and oven drying treated with different resins

Hence, the resin used in treatment has a significant effect on the ASE values. These differences might be explained by compatibility between the modification agent and wood, the ability of molecules to penetrate the cell walls, and by different allocation (retention) of resin across the specimen.

As can be seen from our correlation plots, Figures 2a and 2b, it appears that the improvement in the dimensional stability of treated wood is caused both by the increased WPG and cell wall bulking effect. A weak correlation between WPG and ASE was found, Figure 2a, because at the same WPG large difference in ASE were observed. In contrast, a high correlation between dimensional stability and cell wall bulking (resin located in the cell wall micro-voids) was found which can be useful in predicting dimensional stability even before the ASE tests are conducted, or, reduce (or even eliminate) the amount of measurements during the test.

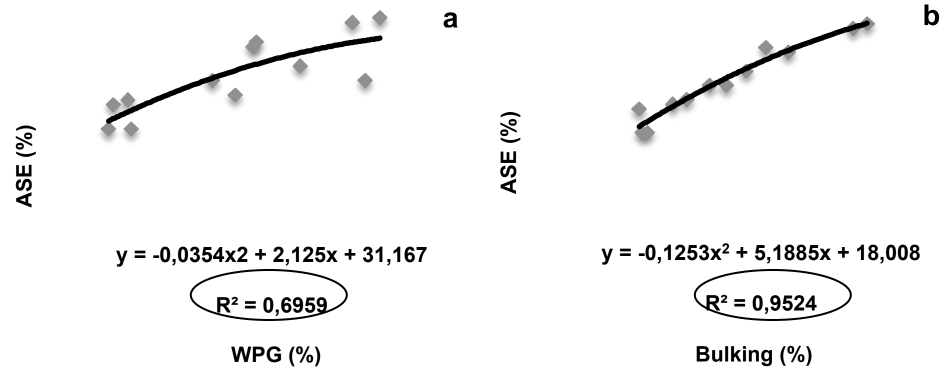

Figure 2: a) correlation between WPG and ASE and b) between Bulking and ASE

The high correlation between ASE and bulking can be explained by regions accessible to water which are partly occupied by resin and increased rigidity of the cell wall, which results in lower swelling.

Stamm in 1964 already demonstrated the impact of the size of molecules on their ability to penetrate into the wood cell walls. He found, that when increasing the size of the molecule in the liquid, the rate of swelling of the cell wall due to reduced diffusion, decreases. However, Mantanis *et al.* (1994), Gindl *et al.* (2002), Furuno *et al.* (2004) showed that molecules such as pyridine, benzalcohol, melamine monomer, PF resin monomer and oligomers (molecular weight 79, 108, 126 and from 107 to 290) are able to swell the cell wall significantly.

Our results, shown in Figure 3, prove that by using a resin with a defined size of molecule, the amount of modification agent can be reduced by about 70% to achieve an equal improvement in the dimensional stability of beech wood.

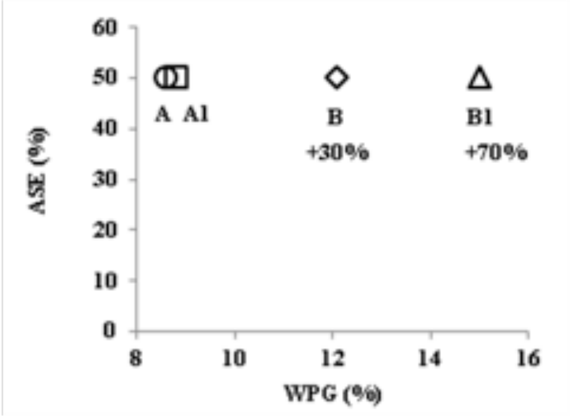

Figure 3: Different WPG of resins to achieve ASE of 50%

CONCLUSIONS

The dimensional stability was assessed on beech wood treated with different average molecular size of PF resin oligomers. The positive effect of PF resin treatment on the dimensional stability of beech wood (as we expected) was confirmed and comparatively constant dimensional stability during cyclic tests was observed. Good correlation between molecular size and an improvement in dimensional stability was achieved. Our results from the treatment optimisation confirmed that it is possible to reduce WPG and achieve the same ASE in beech wood.

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Wood-Water Relations of Oil-Heat-Treated Poplar Wood

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Keywords: oil-heat-treatment, poplar, sorption, diffusion

ABSTRACT

In this study the sorption rate and the diffusion coefficient of Oil-Heat-Treated (OHT) Pannonia Poplar (*Populus* × *euramericana* cv. Pannonia) wood without coating was investigated. The treatment temperature was 200°C, with a 6 hour treatment time. Moisture uptake rate (in %/h) at T= 20°C, φ= 65% was tested with 0% initial moisture content. The diffusion coefficient was measured with the dry-cup test according to EN ISO 12572. The decrease in the moisture uptake rate was only apparent. Momentary moisture contents divided by the equilibrium moisture contents did not show significant differences between untreated and OHT samples at the time points investigated. Equilibrium moisture content was reached by all samples in the same amount of time; therefore the decreased moisture uptake rate in OHT wood is due to a decrease in water storage capacity. Moisture transport through the untreated samples was significantly higher compared to the heat treated samples in both the radial and tangential directions. As a result of the heat treatments, diffusion decreased by ~65% in the tangential and ~80% in the radial direction. Diffusion in untreated material was lower in the tangential direction compared to the radial direction. In the case of the heat treated samples these differences were reduced or the trend between the anatomical directions was reversed. The effect of the treatment medium was not clear, this means that the oil uptake and the thin oil layer on the surface does not have a significant effect on diffusion in heat treated wood.

INTRODUCTION

Pannonia poplar has favourable material properties (air dry density 406 kg/m^3, MOR 72 MPa, and MOE 7590 MPa), and shows a high growth rate among cultivated poplars in Europe (Komán and Fehér 2010). Therefore, it is important to investigate its properties and utilization possibilities. Moisture uptake in wood occurs through diffusion and capillary flow. Below the fibre saturation point moisture water can be transported as vapour in the lumens, or as bound water in the cell walls though diffusion. In this phase, moisture movement can be modelled successfully with a diffusion front moving through the wood, causing smooth moisture content gradients in the different cardinal directions (Droin-Josserand et al. 1988). However, in reality moisture transport in wood is suspected to be more difficult. The characteristics of heat-treated woods' sorption behaviour usually includes a slower reaction to changes in relative humidity than in natural wood. Therefore, the sorption should be lower and slower (Pfriem et al. 2007).

EXPERIMENTAL

Poplar (*Populus × euramericana* cv. Pannonia) wood was oil-heat-treated (OHT) in linseed oil. The dimensions of the treated samples were 18×40×220 mm (T×R×L). The treatments were performed at a temperature of 200°C, with 6 hours duration. As a control treatment to determine the effect of oil uptake on the diffusion properties, a steam-heat-treatment (SHT) (T=180°C, t= 4 hours) was used.

The sorption rate of OHT wood without coating was tested. Moisture uptake rate (in %/h) at T= 20°C, φ= 65% was tested with 0% initial moisture content. 40×18×15 mm (R × T × L) samples were cut from the OHT laths. Untreated samples served as control. The samples were dried at 105°C until constant mass and then weighed. Thereafter, the samples were stored in a climatic chamber until reaching constant mass and weighed at assigned times (4, 8, 24, 48, 72, and 172 hours) after being placed in the climate chamber.

Water vapour flow rate was measured with the dry-cup test according to EN ISO 12572. OHT and steam-heat-treated material was tested, with untreated specimens serving as a control. The thickness of the samples was 10mm, with a diameter of 88mm. The samples had clear radial or tangential surfaces. Calcium-chloride was used as a desiccant to ensure 0% relative humidity (RH) in the testing cup. The cups were placed in a climatic chamber set to T=20°C and φ =65%. The cups were weighed once a day to determine the mass of moisture transported through the specimens.

RESULTS AND DISCUSSION

Sorption test

The moisture content of heat-treated specimens was lower at all of the time intervals investigated, compared to the untreated wood. The change in the moisture content of the oil heat-treated wood showed some similarity to that of the untreated wood, since after 48 hours the moisture content increased only slightly, and all specimens were close to the equilibrium moisture content (EMC) (Figure 1). Heat-treated samples adsorb less moisture during the same amount of time than untreated ones, but saturation of OHT and untreated wood occurs in the same duration.

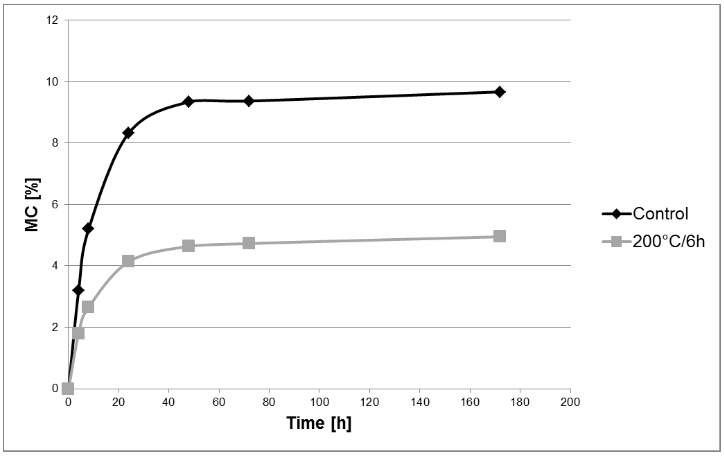

Figure 1: Changes in moisture content of oil heat-treated and untreated poplar wood at normal climate (T= 20°C, φ= 65%) as a function of time (Treatment medium: linseed oil)

The moisture uptake rate was the highest during the first 4 hours (Figure 1). The moisture uptake rate had already significantly decreased in the second 4-hour interval. In the last period (near to EMC) moisture uptake was minimal, as there were no significant differences between untreated and OHT wood. These results show that when investigating the first short period, the moisture uptake of OHT wood lags far behind that of the untreated wood. Since saturation occurs in the same time in both natural and heat-treated wood, it is revealed that the decrease in the moisture uptake rate in OHT wood is due to the decrease in water storage capacity.

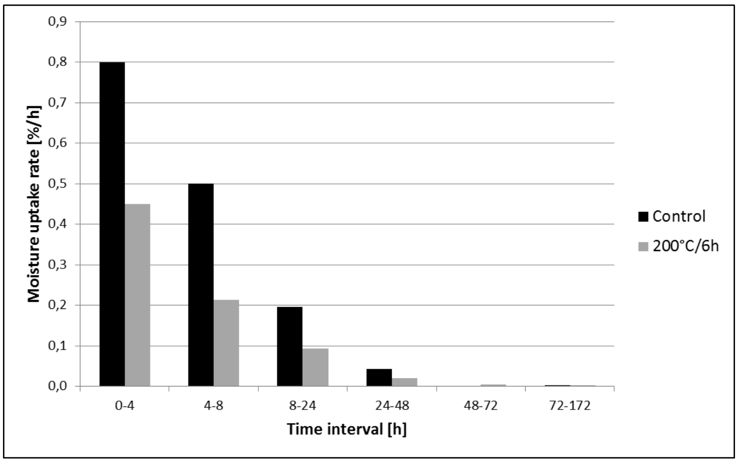

Figure 2: Moisture uptake rates at normal climate (T= 20°C, φ= 65%) for the investigated periods

However, a decrease in moisture uptake rate is only apparent. By dividing the reduced EMC (due to OHT treatment) by the momentary MC, no significant differences can be found between untreated and OHT samples at the time points investigated (Figure 3). This result also shows that the apparent decrease in moisture uptake rate is due to the reduction in the amount of sites which are able to bind with water molecules. Namely, the water binding capacity decreases, not the water binding capability. Apart from that, under changing climatic conditions the use of heat-treated wood is preferable.

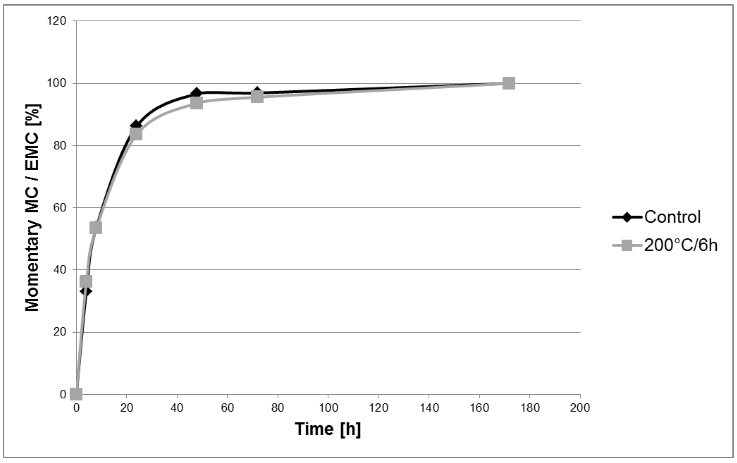

Figure 3: Saturation of samples at normal climate (T= 20°C, φ= 65%) as a function of time

Diffusion test

In general, in both the radial and tangential directions, the moisture transport through the untreated samples was significantly higher than in the heat treated samples. As a result of the heat treatments, diffusion decreased ~65% in the tangential and ~80% in the radial direction. The effect of the treatment medium was not clear because in radial and tangential directions (Figure 4), the density of the moisture flow rate was similar for both OHT and SHT wood. This means that the oil uptake and the thin layer of oil on the surface does not have a significant effect on diffusion in heat treated wood.

Water diffusion in untreated material was lower in the tangential direction compared to the radial direction. After heat treatment these differences were reduced or reversed. One reason for the wood being more water vapour resistant as a result of heat treatment could be the decreased hygroscopicity and equilibrium moisture content. These phenomena decrease the moisture content difference between the two surfaces of the wood which are exposed to different climatic conditions (in this case 0% and 65% RH). Thus, the moisture gradient becomes smaller.

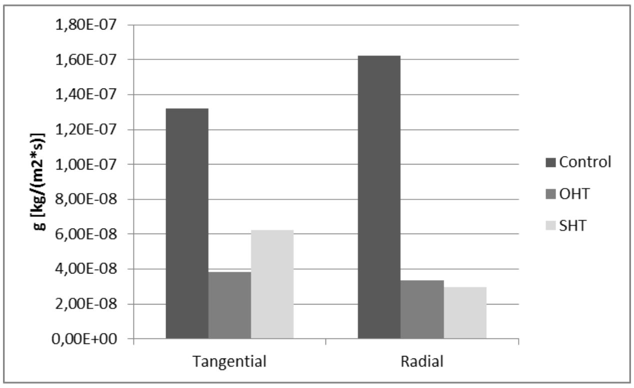

Figure 4: Density of water vapour flow rate in tangential and radial directions

CONCLUSIONS

The decrease in moisture uptake rate due to OHT was only apparent. Momentary moisture content divided by the equilibrium moisture content did not show significant differences between untreated and OHT samples at the time points investigated. The equilibrium moisture content was reached by all samples in the same amount of time; therefore the decrease in moisture uptake rate in OHT wood is due to the decrease in water storage capacity. Moisture transport through the untreated samples was significantly higher compared to the heat treated samples in both the radial and tangential directions. The effect of treatment medium (steam or hot oil) was not clear, this means that the oil uptake and the thin oil layer on the surface does not have significant effect on diffusion in heat treated wood.

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Effect of Wood Modification on Water Related Properties and Penetration of Adhesives into Scots Pine and Beech

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Keywords: fluorescence microscopy, gross penetration, modified wood, water uptake, wetting

ABSTRACT

The water related properties and penetration behaviour of three coldset wood adhesives into different modified materials were studied using a capillary water uptake test, contact angle measurement and fluorescence microscopy. The contact angle data revealed an increase in the hydrophobicity of the wood surface by all modifications except heat treated wood. Different modification intensities had no effect on contact angles. All modifications led to a notable decrease in water uptake in every anatomical wood direction. The results of the fluorescence microscopy provided good knowledge on the penetration behaviour of two waterborne and one moisture curing gluing systems into the different types of modified wood, indicating different manners of penetration based on the modification system used and the adhesive type.

INTRODUCTION

Wood modification aims to improve different practical characteristics of wood such as durability, dimensional stability and its weathering performance (Hill 2006). Beside these advantages, for example in bulk treatments, modification alters the anatomical features of the wood by blocking pathways with resins or treatment solutions which may impede the further flow of water into the wood tissue. It also changes the chemical composition of the wood e.g. by losing free hydroxyl groups during heat treatment or other chemical modifications (Kamdem *et al*. 2002, Mai and Militz 2004), which affects the water related properties and hydrophobicity of the wood and hence its gluing properties. It is known that less polar and in some cases less porous modified wood surfaces can result in a diminished bonding performance arising from the reduced adhesive wetting of the wood (Hunt *et al.* 2007). The objective of this work was to study the wetting characteristics of different types of modified woods by measuring the contact angle of water droplets on the surfaces of furfurylated and N-methylol melamine (NMM) treated Scots pine, and heat-treated Scots pine and beech and also the evaluation of water uptake into these modified materials. Then, as a second step, the gross penetration of three conventional wood adhesives into the wood structure was determined using fluorescence microscopy to examine the effect of modification on the penetration of the resins used.

EXPERIMENTAL

The furfurylation of Scots pine (*Pinus sylvestris* L.*)* was carried out through an impregnation process by Kebony ASA (Norway) with two concentrations of furfuryl alcohol industrially named Kebony FA 40 and FA 70, with 65% and 75% weight percent gain (WPG) respectively. The melamine treatment of Scots pine was performed with a full cell process using solutions of 10%, 20% and 30% concentration of N-methylol melamine (NMM) resin Madurit MW840/75WA (Ineos Melamines GmbH, Frankfurt, Germany). Heat-treatment was done on both Scots pine and beech at 195 and 210°C by Timura Holzmanufaktur GmbH (Südharz, Germany) with the industrial scale vacuum-press dewatering method (Vacu^3). The sessile drop water contact angles on the tangential and radial surfaces of planed samples were measured with a G 10 device (Krüss GmbH, Hamburg, Germany) and DSA 1 software. In each case 20 measurements were performed. The droplet volume was 10 µl and the contact angle value was taken 5 s after droplet deposition. In accordance with DIN 52617 and using ten replicates for each treatment and direction, the capillary water uptake (CWU) was measured along the longitudinal direction of samples of 20 × 20 × 200 mm^3, and along the tangential and radial directions of samples of 40 × 40 × 40 mm^3 (R × T × L). Emulsion polymer isocyanate (EPI), poly vinyl acetate (PVAc) and one-component moisture curing polyurethane (PU) adhesives (Jowat AG, Detmold, Germany) were spread on the tangential surfaces of wood samples by hand brushing and the samples were left aside for 1 week at room temperature, thus allowing the adhesives to penetrate as much as possible. Microscopic sections with 40-µm thickness were prepared from the transverse surface of glued samples. The sections were stained with a drop of 0.5 % safranin O solution followed by washing of the sections with water and ethanol. An Eclipse 50i fluorescence microscope equipped with appropriate filter sets, a Sight DS-5M-L1 digital camera and NIS-Elements F software for image analysis were used to examine sections (all Nikon, Düsseldorf, Germany). Using random areas of penetrated adhesive, the radial effective penetration (EP) of the glues into wood structure was measured according to the definitions of Sernek *et al.* (1999) following Eqn. 1.

$$\mathrm{EP} = \frac{\sum_{\mathrm{i}}^{\mathrm{n}} \mathrm{Ai}}{\mathrm{Xo}} \tag{1}$$

where EP = effective penetration, µm; Ai = area of adhesive object i, µm^2; n = number of objects; Xo = width of the maximum rectangle determining the measurement area (1100 µm).

RESULTS AND DISCUSSION

Contact angle data indicated increased hydrophobicity of the wood surfaces after furfurylation, especially in the case of the tangential surfaces (Table 1). An exception was found for the radial surface of FA40 furfurylated wood which could be due to the presence of hygroscopic buffering salt agents used in the furfurylation process. A significant increase in hydrophobicity was also noted for the NMM treated wood which was independent of the NMM resin load. The radial surfaces presented higher contact angles and thus a lower wetting force. With the exception of the tangential surface of beech, the wetting of the wood surfaces was negatively affected by heat-treatment mainly due to the migration of extractives to the wood surface and chemical changes of the wood structure after heat treatment. For both species no major differences were detected in contact angles with the treatment temperature (195 and 210 °C) and between the radial and tangential surfaces.

Table 1: Measured contact angles for furfurylated Scots pine (FA 40 and 70), NMM modified Scots pine (10%, 20% and 30% NMM), and heat-treated Scots pine (HT-S) and beech (HT-B)

Contact angle [°]	**Scots pine-control**	**Beech-control**	**FA 40**	**FA 70**	**10% NMM**	**20% NMM**	**30% NMM**	**HT-S 195°C**	**HT-S 210°C**	**HT-B 195°C**	**HT-B 210°C**
Radial	69.2	72.1	61.3	79.7	83.9	84.6	84.2	86.1	81.4	80.5	83.1
SD	21.8	9.1	22.7	11.7	9.8	9.4	13.8	11.9	9.7	9.9	13.2
Tangential	47.0	77.9	68.0	79.8	76.2	74.6	66.7	81.7	79.8	73.2	79.5
SD	21.0	14.6	28.3	16.4	9.2	12.7	16.6	15.5	13.1	12.6	14.3

As shown in Figure 1 and as expected, in all cases, the highest CWU was gained in the longitudinal direction. CWU decreased in all three of wood's anatomical directions after each of the modifications. In the case of the NMM treatment, the maximum effect of the modification was found in the CWU in the tangential direction and lowest in the longitudinal direction. The concentration of the treatment solution had no effect on the reduction in CWU. The lower water uptake of the NMM treated wood can be explained by the penetration of NMM resin in the different morphological regions of the wood tissues and into cell walls and the occlusion of the main penetration pathways for water, e.g. lumens of axial elements (tracheids, vessel elements) and ray cells by the resin. The CWU of wood also decreased after heat treatment owing to degradation of the wood polymers (probably due to destruction and deacetylation of hemicelluloses and to an increase in cellulose crystallinity and new lignin networks).

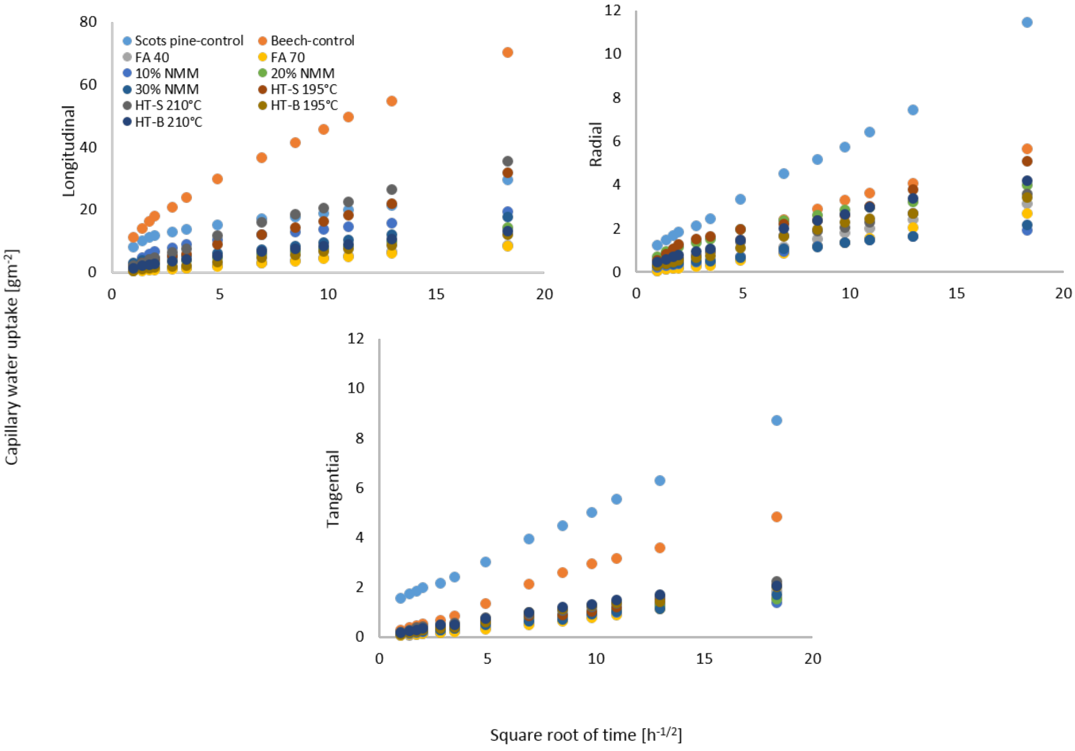

Figure 1: Water uptake along longitudinal, radial and tangential directions

Measurement of the effective penetration (EP) showed the negative effect of furfurylation only in the case of EPI into the FA70 treated samples, whilst an improved EP was noted for PVAc (Figure 2). The EP of PU and EPI reduced after NMM modification but again the EP of PVAc increased after 10% and 20% NMM treatment. In the case of Scots pine, the EP of all adhesives improved by increasing the treatment temperature while for beech, an increase in EP was seen for PU and PVAc in the case of samples treated at 195 °C.

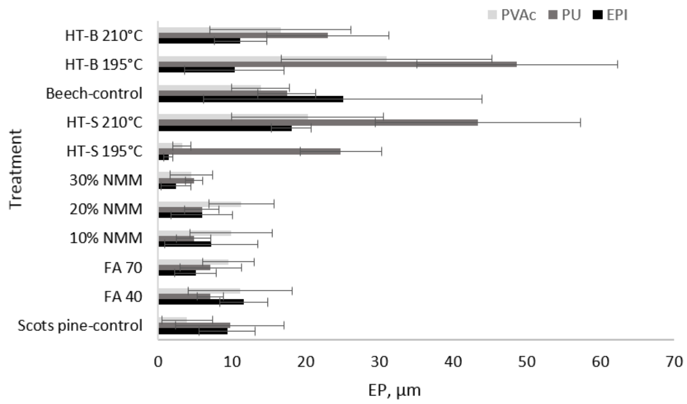

Figure 2: Effective penetration (EP) of adhesives in the radial direction of different wood types

CONCLUSIONS

The results from contact angle measurement and capillary water uptake tests gave a better insight into the surface property and hygroscopic behavior of modified wood and the gross adhesive penetration test provided good knowledge on the interaction between three common wood adhesives and different modified wood tissues. The results obtained are useful in predicting the adhesion properties of modified wood required for its wise use in wood structures.

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Accelerated Weathering of Thermally Modified Wood Finishing with Waterborne and UV-Curable Coatings

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Keywords: coating performance, glossiness-color stability, FT-IR, hydrothermal wood surface

ABSTRACT

One of the most remarkable aspects of hydrothermal wood is its darker color compared to natural timber. To maintain the aesthetic features of thermally modified products during outdoor use it is necessary to protect it against natural weathering factors and thus avoid degradation and changing the tones of exposed surfaces. Finishing processes with waterborne and UV-curable coatings were applied to Thermo-Oak (*Quercus robur*). Following surface coating, the samples were subjected to an accelerated weathering test (Solarbox chamber M/S Erichsen, model 522) with changing UV radiation cycles, condensation and water spray to simulate conditions of temperature, direct solar radiation and precipitation. All samples were examined after each aging cycle to monitor the color changes using visible light reflectance spectroscopy and the CIELab system. In addition, the gloss value, contact angle and surface changes by FT-IR were measured. The results indicated that finishing hydrothermal wood with waterborne and UV-curable coatings improves the surface resistance, thus increasing the service life of wood products in outdoor uses by avoiding aesthetic changes over time. Finishing with waterborne coatings improved the photostability after accelerated weathering test with steady color and gloss values after several cycles. On the other hand, samples finished with UV-curable coatings showed higher color shade variations and gloss loss, but the surfaces maintained acceptable protection values. With regard to the hydrophobicity test, the coated surfaces maintained high values of contact angle in concordance with the features of hydrothermal wood. The FT-IR spectra of the coated surfaces do not present significant differences over aging time, indicating the suitable adhesion of coatings to the wood surface.

INTRODUCTION

Through hydrothermal treatment a range of color options can be achieved in many species without the use of stains. Aesthetically the wood becomes darker in color and it brings a striking appearance to lighter colored wood species. Besides color changes, the treatment reduces the moisture content of wood species allowing their use in outdoor or wet environments, increasing the service life of wood and wood-based materials. On the other hand, the modified wood surfaces exposed in service could present drawbacks in terms of visual alterations, such as color changes, wear and flaking, caused by weathering (Lis *et al.* 2009). Finishing wood with coating products has proved itself to be a good option to reduce the weathering effects and to maintain a homogeneous color when the material is exposed outdoors in different directions or designs.

EXPERIMENTAL

The wood of common oak (*Quercus robur*) was thermally modified according to industrial production standards at 170 ºC (Termogenik®, Spain) in a heat-treatment chamber in the presence of steam for a period of 60 h. The finishing process of the thermally modified samples was carried out with two types of coatings: UV-curable coatings (50 g m^{-2}) using industrial rollers in a hybrid line mix of LED and arc lamps (in the Sherwin-Williams Company) and waterborne coatings (210 g m^{-2}) applied using a brush under laboratory conditions. Untreated samples of common oak were used to compare all analytical characterizations. After wood finishing, the samples were exposed to an accelerated weathering test (Solarbox chamber M/S Erichsen, model 522) to simulate conditions of temperature, solar radiation and precipitation. Each cycle was completed with 112 min of radiation at 70 ºC using UVB-280 lamps followed by18 min of condensation. The changes in color (measured by UV-Visible spectroscopy and the CIELab system), gloss, contact angle and surface chemistry (by FT-IR) were examined in all samples after every 5 aging cycles (up to 20). Table 1 summarizes the finishing settings and the surface measurements.

Table 1: Coating parameters and evaluation methods

Sample	**Coating**	**Finishing method**	**Drying**	**Curing**	**Surface changes**				
					Color		Gloss	Wettability	Coating
Thermo-Oak (170 ºC)	Waterborne	Brush (*Laboratory*)	YES	-	*VLRS*[1]	*CIE Lab*[2]	*GM*[3]	*CA*[4]	*FT-IR*[5]
	UV-curable	Roller machine (*Industry*)	-	YES					

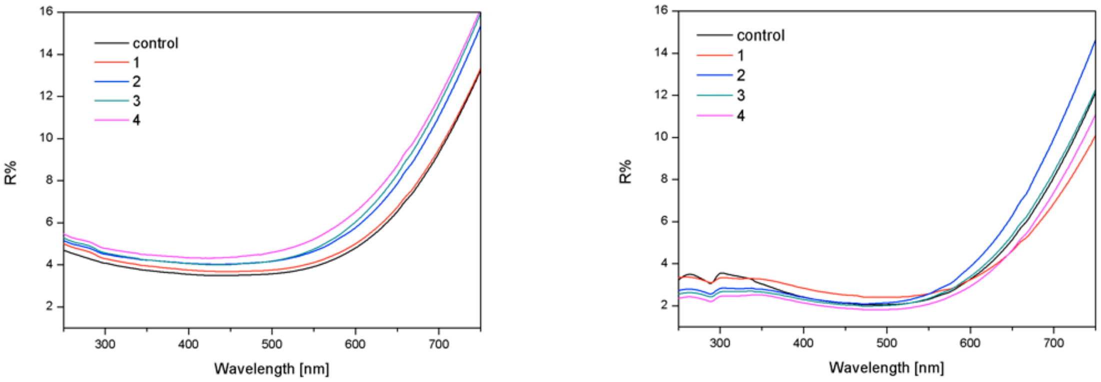
*[1] Visible Light Reflectance Spectroscopy;[2] CIE method L*a*b*;[3] Gloss-meter measurement;[4] Contact Angle; [5] Fourier Transform-Infrared Spectroscopy*

RESULTS AND DISCUSSION

After the weathering test the coated Thermo-Oak samples retained their properties, thereby improving the surface resistance, avoiding aesthetic differences over time and increasing the service life of the wood products in outdoor uses. Table 2 shows that the color difference ($\Delta E_{ab}*$) after 20 cycles was more pronounced in the UV-curable finishes changing by 2 units, though this is considered to be minor fading (Podgorski *et al*. 2011). A similar trend is shown for Chroma ($C_{ab}*$) and hue (h) with no general differences in saturation in both coated surfaces. The UV-Vis reflectance spectrum (Figure 1) revealed a curve in the waterborne finishes with differences in some intervals (340 to 380 nm and longer than 500 nm) probably due to brightness and yellowing values. In the case of the UV-curable finishes, an analogous tendency was discernable in all spectra. During the weathering test the gloss values in the waterborne surfaces decreased by up to 10%, meanwhile in the UV-curable surfaces the increase was up to 10%. The hydrophobicity in the waterborne surfaces remained stable over the cycles but in the UV-curable surfaces it decreased by approx. 15 % after 20 cycles (Table 3). The surface tension decreased with waterborne and increased with UV-curable coatings and an inverse relation could be established between the work of adhesion (W_a) and surface tension where the higher W_a corresponds to the lower surface tension (Hochmanska *et al.* 2014).

Table 2: Optical measurements of finished thermo-oak after weathering test

Sample	**Coating**	**Aging cycles**	**Color**			**Gloss**
			ΔE_{ab} *	**C_{ab}***	**h**	**60°**
Thermo-Oak (170 ºC)	Waterborne	Control	-	8.99	40.38	53.50
		5(1)	0.49	8.6	40.26	53.30
		10(2)	0.9	9.32	41.89	52.30
		15(3)	1.03	9.45	42.46	49.90
		20(4)	1.63	10.04	43.29	47.70
	UV-curable	Control	-	9.73	36.07	4.10
		5(1)	0.76	9.77	36.97	4.20
		10(2)	0.85	9.75	37.09	4.50
		15(3)	1.19	10.02	37.23	4.60
		20(4)	2.1	11.11	38.54	4.60



UV-curable **Waterborne**

Figure 1: UV/Vis reflectance spectra of coated surfaces

Table 3: Values of contact angle and surface tension after weathering test

Sample	**Coating**	**Aging cycles**	**Contact angle[1] [º]**			**Surface tension** [mJ/m^2]
			water	diiodomethane	Ethylene glycol	
Thermo-Oak (170 ºC)	*Waterborne*	Control	72.3±2.1	60.8±0.9	71.2±1.1	31.7
		5	69.2±1.2	57.4±0.7	69.9±1.0	33.7
		10	69.0±1.2	60.5±0.6	71.3±0.9	32.9
		15	70.7±1.5	56.7±0.8	70.4±1.4	33.2
		20	69.6±1.1	57.9±0.8	71±0.8	33.2
	UV-curable	Control	63.1±3.1	40.9±0.7	50.8±0.9	41.4
		5	61.9±2.1	48.9±0.4	48.8±0.7	42.7
		10	60.4±1.4	46.7±0.7	44.6±0.9	44.5
		15	57.7±2.1	49.7±1.3	51.4±1.0	43.4
		20	53.9±1.5	59.1±0.6	53.2±1.6	43.3

[1] *Average value of five measurements*

The FT-IR analyses of the coated surfaces revealed that the waterborne coating was more stable and should be the most durable during the weathering test. However, it was evident that the thickness of layers and the transparency of the products influence the results, but eventually photodegradation of wood surface may occur. The UV-curable coatings exhibited a decrease in its peaks over time, but still they are considered to be effective coatings from an economic and aesthetic point of view.

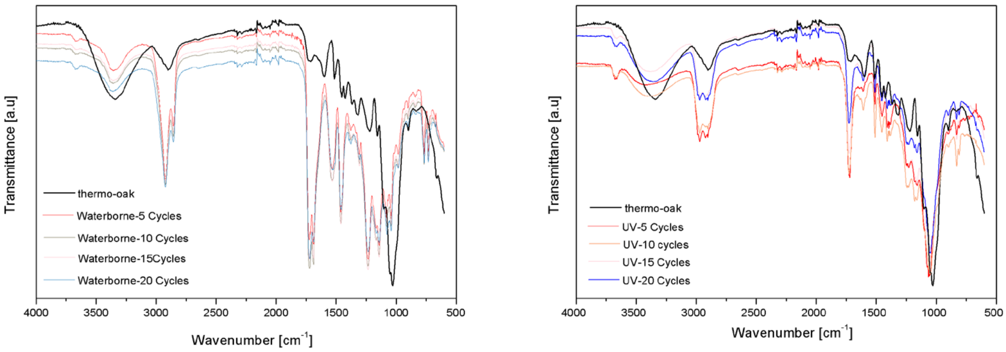


Figure 2: FT-IR analysis of coatings after weathering test

CONCLUSIONS

Finishing with waterborne and UV-curable coatings prevents Thermo-Oak from the effects of natural weathering and helps to avoid degradation and changing tones in outdoor uses. Although UV-curable coatings showed more pronounced surface degradation and decreased hydrophobicity, the acceptable protection of color and gloss were maintained. On the other hand, waterborne coatings improved the photostability after accelerated weathering test with steady color, gloss and hydrophobicity after aging cycles, though using higher amounts of products.

ACKNOWLEDGEMENTS

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Ammonia Treatment of Light-irradiated Wood

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Keywords: ammonia treatment, colour, IR spectra, light-irradiation

ABSTRACT

This study deals with the ammonia treatment of light-irradiated wood. The colour of light-irradiated wood changed to a greater extent than that of unirradiated wood with ammonia treatment. The carbonyl groups decreased and the amine groups increased with ammonia treatment. The carbonyl groups which increased by light-irradiation also decreased with ammonia treatment.

INTRODUCTION

The coloration method for wood by ammonia treatment has been well known for a long time (Tinkler 1921). Ammonia treatment, as well as the thermal modification of wood, is applied to modify the surface colour of wood. Higashino and Nakano (1985) carried out ammonia treatment on 48 species grown in Iwate Prefecture, Japan, and investigated the discoloration of ammonia treated wood by light-irradiation. Badoni *et al*. (1990) reported the effects of ammonia on the surface colour and figure of 51 Indian timbers. Weigl *et al*. (2007) showed that ammonia fuming could be an effective way of pre-aging wood, resulting in stabilized colour in some species. Miklečić *et al*. (2012a) reported that ammonium-treated oak wood showed better stability to discoloration than heat-treated material. Miklečić *et al*. (2012b) showed that the fuming of oak resulted in the greatest reduction in tannin content. However, it was established that tannin had no major influence on colour changes in maple and larch wood in the ammonia-fuming process. Weigl *et al*. (2012) discussed not only the colour changes but also some physical and mechanical properties such as equilibrium moisture content, density, bending strength, bending stiffness, and impact bending strength. Weigl *et al*. (2009) reported that the anisotropy of swelling and shrinkage increased due to ammoniation.

Although there are many reports on the changes in properties of wood with ammonia treatment, there are no reports on the changes in colour of light-irradiated wood with ammonia treatment.

This study discusses the change in wood colour and DRIFT spectra resulting from ammonia treatment after light-irradiation.

EXPERIMENTAL

Materials

The specimens used in this study were Japanese cypress (*Chamaecyparis obtusa*) and Japanese beech (*Fagus crenata*) having dimension of 50 ×10 × 1 mm^3 in longitudinal, radial, and tangential directions, respectively. Before treatment, all the specimens were extracted in ethanol for 16 hours using a Soxhlet apparatus and dried under vacuum at 40 °C. The colour parameter before treatment are shown in Table 1.

Table 1: The colour of specimens before treatment

Species	*L**	*a**	*b**
Japanese cypress	82.40 ± 0.23	1.62 ± 0.10	20.31 ± 0.22
Japanese beech	68.02 ± 0.47	6.17 ± 0.53	17.69 ± 0.20

Light-irradiation as a pre-treatment

Before ammonia treatment, the specimens were irradiated with a xenon lamp at 180 Wm^{-2}, in the range of 300 – 400 nm, at 63 °C (black panel temperature) and 50%RH for 50 hours in a commercial chamber (SX-75: Suga Instruments Co. Ltd., Japan).

Gas phase ammonia treatment

After light-irradiation, the specimens were treated in a desiccator over a 28% ammonia solution for 30 hours.

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 1900 cm^{-1} and 850 cm^{-1}, the height of the band at 1374 cm^{-1} due to CH deformation in polysaccharides was used as an internal standard (Kataoka and Kiguchi 2001, Mitsui *et al*. 2004, Mitsui and Tsuchikawa 2005).

Colour measurement

The colour of the surfaces of the specimens was measured with a colorimeter (SE-2000: Nippon Denshoku Industries Co. Ltd., Japan). The sensor head was 6 mm in diameter. Measurements were made using a D_{65} illuminant and a 10° observer. The tristimulus values X, Y, and Z of all specimens were obtained from the colorimeter and the CIELAB colour parameters (L^*, a^* and b^*) were then computed.

RESULTS AND DISCUSSION

Colour changes

Fig. 1 shows the changes in colour of Japanese beech by ammonia smoking. The L^* of unirradiated specimen decreased by ammonia fuming. This result agrees with previous reports (Higashino and Nakano 1985, Miklečić *et al*. 2012b). On the other hand, the L^* of light-irradiated wood was remarkably decreased by ammonia smoking in comparison to that without light-irradiation. The trend in the changes in the colour of Japanese cypress was similar to that of Japanese beech. The a^* of light-irradiated beech decreased by ammonia treatment. The a^* of light-irradiated Japanese cypress increased to a greater extent to that of the unirradiated one with ammonia treatment. The b^* of both species increased with light-irradiation, and it was decreased by ammonia treatment after light-irradiation. These trends in colour change were similar to those of light-irradiated wood with heat treatment (Mitsui *et al*. 2001, Mitsui *et al*. 2004, Mitsui 2004).

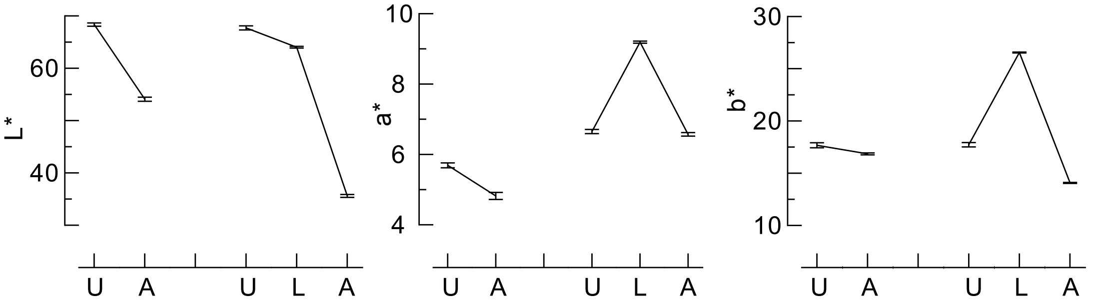

Figure 1: Changes in colour of Japanese beech. U: untreated, L: light-irradiation for 50 hours, A: ammonia fuming for 30 hours

IR changes

Fig. 2 shows the changes in the IR spectra of Japanese cypress by ammonia treatment. On the unirradiated wood, the carbonyl group (1,737 cm^{-1}) decreased and the amine group (1,650 cm^{-1}) increased with ammonia treatment (Fig.2(a)). These results agreed with previous ones (Miklečić *et al.* 2012b). The carbonyl groups (1,737 cm^{-1}) increased and lignin skeletal (1,510 cm^{-1}) decreased with light-irradiation (Fig.2 (b)) as in previous reports (Kataoka and Kiguchi 2001, Mitsui *et al.* 2004, Mitsui and Tsuchikawa 2005). The carbonyl groups (1,737 cm^{-1}) which increased by light-irradiation, decreased by ammonia treatment. The amine groups (1,650 cm^{-1}) of light-irradiated wood increased by ammonia treatment in the same way as that of unirradiated wood. The increment of amine groups (1,650 cm^{-1}) in irradiated wood was greater than that of unirradiated one. Therefore it was thought that ammonia gas reacted with carbonyl groups.

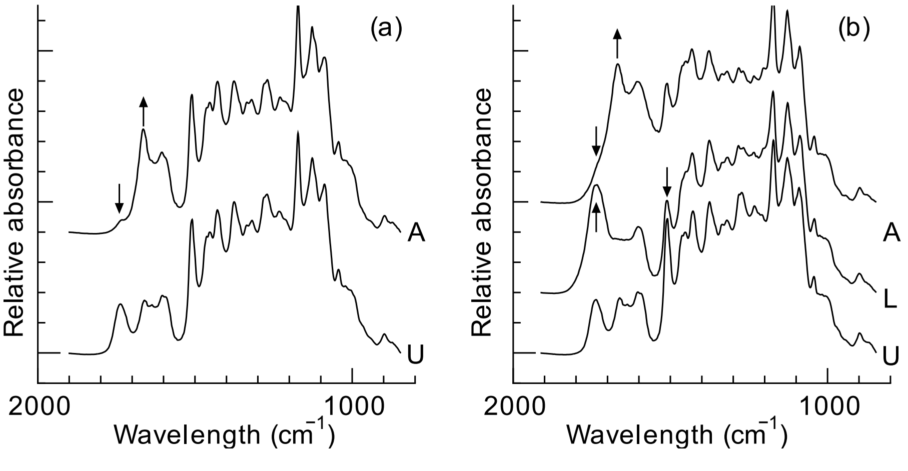

Figure 2: Changes in IR spectra of Japanese cypress. U: untreated, L: light-irradiation for 50 hours, A: ammonia fuming for 30 hours

The trends in the changes in colour of light-irradiated wood by ammonia treatment were similar to those of light-irradiated wood by thermal treatment. However, the trends in the changes in IR spectra of light-irradiated wood by ammonia treatment differed to those of light-irradiated wood by heat treatment. Therefore it was guessed that the chromogenic mechanism would differ between the ammonia treatment and thermal treatment for light-irradiated wood.

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Influence of Duration of Ammonia Treatment on Wood Colour Stability to UV Light

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Keywords: ammonia treatment, colour stability, QUV, tannin

ABSTRACT

One of the methods of modifying the colour of wood and highlighting the wood texture is the modification of wood with ammonia gas. The objective of this work was to establish the influence of the duration of ammonia treatment, and the influence of pre-treatment of wood with tannin in combination with ammonia treatment, on wood colour stability during artificial indoor exposure to UV light. The results of the colour change showed that treatment with ammonia with and without tannin pre-treatment increased the colour stability of the wood samples tested, especially those of spruce and larch.

INTRODUCTION

The colour and colour stability of wood is an appearance-related attribute that could have a significant influence on the consumer's choice of wood furniture and flooring. One of the methods of modifying wood colour and highlighting the wood texture is the modification of wood with ammonia gas. Depending on the duration of modification and the wood properties, the colour can range from light brown to chocolate brown or black. Modification with ammonia gas creates the classic rich warm brown colour and accentuates the ray flecks that is most notable in quarter-sawn white oak (Peipher 2010). The modern industrial fuming technique utilizes environmentally-friendly vacuum-pressure technology that provides good wood fiber saturation and better color intensity over the entire depth of the wood. The colour change obtained is the result of the chemical reaction of ammonia gas with the structural components of wood which is reflected in a change in extractive content, nitrogen content and tannin content (Miklečić *et al*. 2012a). Weigl *et al*. (2009) studied the effect of ammonia fuming on the colour change in 38 wood species and they reported that the greatest colour change was in black locust (*Robinia pseudoacacia* L.) and the least in black walnut (*Juglans nigra* L.). In previous research it has been established that oak wood modified with ammonia gas has better colour resistance to UV radiation than thermally modified oak wood (Miklečić *et al.* 2012b) and that ammonia treatment could be an effective way of pre-aging wood, resulting in stabilised colour in some species (Weigl *et al.* 2007).

The aim of this study was to establish the influence of the duration of ammonia treatment, and the influence of the pre-treatment of wood with tannin in combination with ammonia treatment, on the colour stability of wood during artificial indoor exposure to UV light.

EXPERIMENTAL

Wood samples

Heartwood samples of oak (*Quercus robur* L.), maple (*Acer pseudoplatanus* L.), larch (*Larix decidua* Mill.) and spruce (*Picea abies* L.) wood were used in this study. The wood samples had a radial texture without visible defects and the dimensions were 150 mm x 75 mm x 2.5 mm (L x R x T).

Treatment with ammonia gas

One group of samples was treated with ammonia gas and the other group of samples was first pre-treated with a tannin water solution (5 %) and then treated with ammonia gas. Treatment of wood with ammonia gas was performed with ammonium hydroxide (25 %) for 1, 2, 4, 7, 11 and 16 days in closed plastic chambers in the presence of air at 23 ± 2°C and 50 ± 5% relative humidity. The air volume within the chamber was 0.0135 m^3 to which was added 40 mL of ammonium hydroxide.

Artificial exposure

The artificial indoor exposure was conducted in a QUV tester equipped with UVA-351 fluorescent lamps. Wood samples were exposed to UV light directly at a distance of 50 mm for 384 hours. The temperature of the black panel was (60±2) °C and irradiation was 0.77 W/m·nm.

Colour change

Colour measurements were performed before and after artificial exposure and the overall colour change (ΔE^*) was calculated using the CIE $L^*a^*b^*$ colour measuring system. The measurements were made with a portable spectrophotometer with d/8°measuring geometry, 10° standard observer, D65 standard illuminate and xenon lamp source.

RESULTS AND DISCUSSION

The results of the colour change (ΔE^*) in the untreated and ammonia treated wood samples after 384 hours artificial exposure are presented in Fig. 1. It can be seen that treatment with ammonia gas increased the colour stability of the wood species tested. Moreover, an increase in the duration of ammonia treatment decreased the colour change in spruce and larch wood (Fig. 1c and 1d). Furthermore, in larch wood a linear decrease in colour change can be observed with an increase in the duration of ammonia treatment. Unlike spruce and larch wood, an increase in the duration of treatment had no major effect on the decrease in colour change of oak and maple wood because the most pronounced colour stability was already achieved after one day of treatment with ammonia gas (Fig. 1a and 1b). This could be related to a more intense reaction of maple and especially of oak wood with ammonia after the first day of treatment compared to spruce and larch wood (Miklečić et al. 2012a). A combination of pre-treatment with a water solution of tannin and then ammonia treatment resulted in the greater colour stability of spruce and larch wood compared to ammonia treated wood without pre-treatment (Fig. 1c and 1d). However, in oak wood there was no major difference between the colour change after ammonia treatment either with or without pre-treatment, because of the higher content of tannin compared to the other wood species tested (Fig. 1a). On maple wood the combination of tannin pre-treatment and ammonia treatment showed higher colour stability only on samples with a shorter treatment time (Fig. 1b).

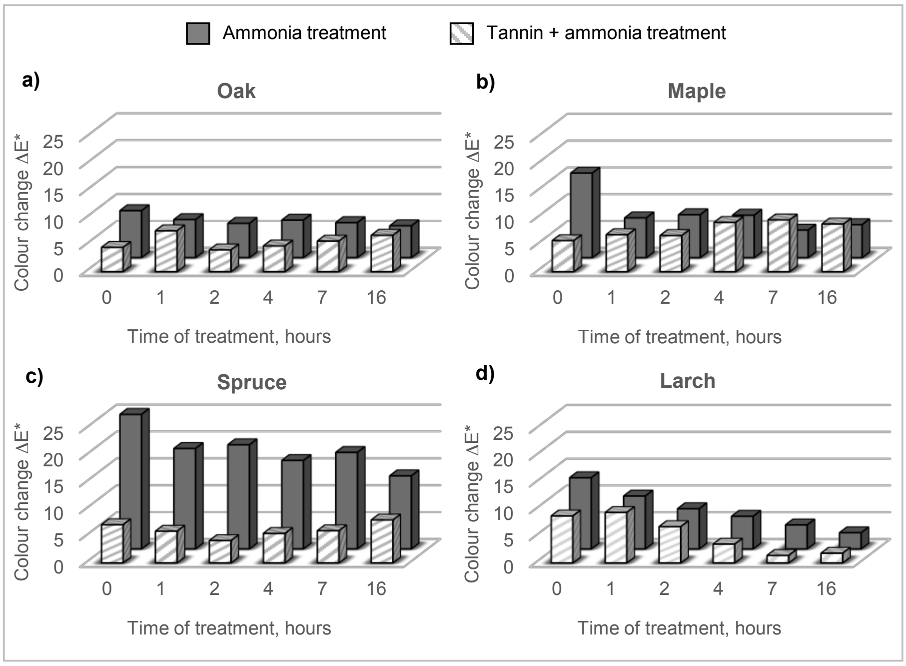

Figure 1: Colour change ΔE* of untreated and wood treated with ammonia gas after 384 hours of indoor artificial exposure

The change in lightness (Δ*L**) had the highest contribution to the overall color change (Δ*E**) after ammonia fuming, compared to Δ*a** and Δ*b**. The results of lightness change in untreated and ammonia treated wood samples after 384 hours of artificial exposure are presented in Fig. 2. The major influence of ammonia treatment on the stabilization of lightness change was observed in spruce and especially in larch wood (Fig. 2c and 2d). Furthermore, pre-treatment with a water solution of tannin and ammonia treatment had a major influence on decreasing the darkening of spruce wood artificially exposed to UV light (Fig. 2c).

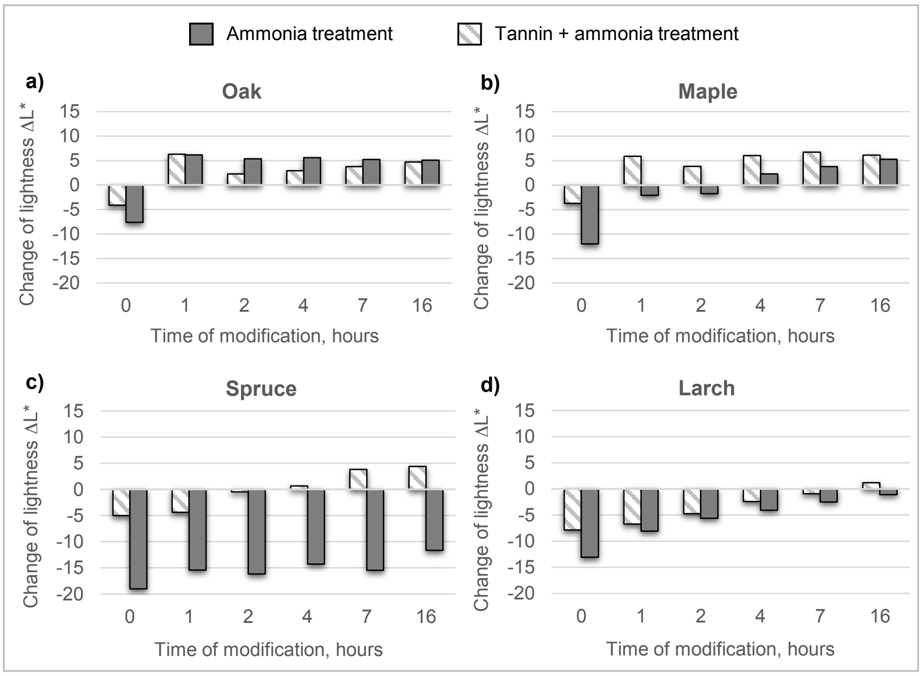

Figure 2: Colour change ΔE* of untreated and wood treated with ammonia gas after 384 hours of indoor artificial exposure

CONCLUSIONS

In this research, the potential of treatment with ammonia gas to increase the colour stability of wooden furniture and flooring can be noticed. Moreover, it was found that extending the duration of ammonia treatment and a combination of tannin pre-treatment with ammonia treatment increases the colour stability of spruce and larch wood as representative of softwoods.

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Different Methods of Nitrogen Analysis and their Suitability to Control the Curing Quality of Wood Modification with Melamine Resin

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Keywords: EN 84, hot water extraction, impregnation, leaching, melamine resin, nitrogen fixation, wood modification

ABSTRACT

To ensure the quality of wood modifications it is important to test the material properties. Moreover, measures of quality control have to assure how the process parameters influence the material properties. A melamine solution was used to impregnate beech wood samples divided into different curing variations including air drying at room temperature. The content of fixed nitrogen after wood modification with melamine resin was tested following two different extraction methods: hot water extraction and leaching (based on EN 84). The fixation after hot water extraction did not show differences between air drying and curing variations. In contrast, leaching the samples did show the influence of different curing temperatures and durations. High fixation rates after leaching ensured proper curing and can be seen as a tool for the quality control of wood modification agents containing nitrogen, such as melamine resin.

INTRODUCTION

Wood modification such as treatment with methylated N-methylol melamine (NMM, referred to as melamine) can be used to improve the performance of non-durable native hardwoods e.g. beech (*Fagus sylvatica* L.) in outdoor applications. A proper melamine treatment consists of two steps: Impregnation and curing. To ensure quality, it is important to test the altered material properties for the desired improvements. Moreover, quality control measures have to be taken to assess how the process parameters influence material properties. Such methods can be: The determination of the solution uptake (SU), Weight Percent Gain (WPG) and the nitrogen fixation (NF). Melamine contains a high percentage of nitrogen, whereas untreated wood is almost nitrogen free (Keller and Nussbaumer 1993). Within the last years, N-fixation after hot water extraction (HWE) has been applied as a quality control method for wood modifications, for example with DMDHEU (Wepner 2006, Krause 2006, Bollmus 2011) and NMM (Mahnert *et al*. 2013). The N-fixation compares the N-content before and after extraction to determine the content of fixed melamine in the sample. The curing reaction of melamine resins is temperature sensitive (Rapp 1999). Proper curing is thus ensured by high temperatures and long curing durations. However, lower temperatures and shorter curing durations are desirable considering economical aspects.

Previously, the authors used NF after HWE to assess the curing quality of a melamine treatment and produced contradictory results: The high fixation after proper curing as well as the low fixation after just air drying were not depicted correctly (Behr *et al*. 2014). Against this background, a new test was set up to further investigate this matter.

The focus of this study was to evaluate if leaching the samples in cold water can be combined with nitrogen fixation to control, and later predict, the curing quality. This method was then applied to evaluate the minimum requirements regarding temperature and duration for a complete curing of melamine resin for the modification of wood.

EXPERIMENTAL

In this study a melamine solution with 19% solid content (INEOS Melamines GmbH, Madurit MW840 75WA) was used to impregnate beech wood samples (25 x 25 x 10mm³) divided into seven curing varieties: Cured at 103 and 120°C for 4, 24 and 48h in drying ovens and one was air dried at room temperature until equilibrium moisture content (EMC) was reached (Table 1).

Table 1: Curing parameters of the melamine treated beech

Temperature [°C]	Duration [h]
120	4, 24, 48
103	4, 24, 48
20 (air drying)	500 (until EMC)

A schematic sequence of the sample preparation is given in Table 2. Samples in group A were ground in a cutting mill (SM 100 by RETSCH Haan Germany with a 2mm sieve) and subsequently fed to the nitrogen analysis (Kjeldahl method in a FoodALYT system by OMNILAB Bremen Germany: Block digestion system SBS 850, steam distillation D 1000 and back titration TS 10) to determine the N-content directly after curing. Entire samples of group B were leached based on EN 84 (tap water instead of demineralized water), dried and afterwards ground up and analyzed for nitrogen. Group C underwent hot water extraction (86°C, 16h), before being dried, ground and analyzed. The calculated nitrogen fixation is the ratio between the nitrogen content of extracted (Ne) and non-extracted (Nne) samples [NF = (Ne/Nne)*100]. The samples of each group were mixed together after grinding. Slight deviations in WPG and therefore nitrogen content between the groups can occur.

Table 2: Sample preparation for N analysis

<table>
<tr><th>Group</th><th>A (N-content)</th><th>B (HWE)</th><th>C (Leaching)</th></tr>
<tr><td>Treatment sequence</td><td colspan="3">Impregnation and curing</td></tr>
<tr><td rowspan="4">⇩</td><td></td><td></td><td>Leaching</td></tr>
<tr><td colspan="3">Cutting mill</td></tr>
<tr><td></td><td>Extraction</td><td></td></tr>
<tr><td colspan="3">Nitrogen analysis</td></tr>
</table>

RESULTS AND DISCUSSION

After impregnation and curing, the solution uptake (SU) and the weight percent gain (WPG) were similar in all groups. The resulting nitrogen contents were also similar after curing/drying (Table 3).

Table 3: Process parameters and results of impregnation (SU), curing (WPG) and nitrogen analysis (N-content and fixation after hot water extraction and leaching)

Max temperature [°C]	Duration [h]	Weight percent gain [%]	(A) Nitrogen content [%]	(B) N-fixation after hot water extraction [%]	(C) N-fixation after leaching [%]
120	4	18.7 (1.8)	7.3	83	91
120	24	18.5 (0.8)	7.5	80	98
120	48	17.6 (0.9)	7.6	78	102*
103	4	19.1 (1.5)	6.9	76	84
103	24	18.6 (0.9)	7.7	77	83
103	48	16.5 (1.2)	7.3	80	98
20 (Air drying)	500	17.9 (1.2)	7.3	81	60
Untreated	-	-	0.15	-	-

* *Higher WPG and therefore higher nitrogen content of group C than group A.*

The first part of the study was to test nitrogen fixation (NF) after two different extraction methods for their accuracy and applicability as a tool to control curing quality. Two extreme curing variations were selected for this comparison: Curing at 120°C for 48h and air drying at room temperature. After hot water extraction (HWE) they had the same fixation, after leaching the cured samples had a high and the air dried samples a low fixation (Table 3). After HWE it was not possible to distinguish between well fixed and unfixed samples. Leaching, on the other hand, did show distinct differences. Therefore, the fixation after leaching will be used to evaluate the curing quality.

The second part was to assess the curing parameters and their influence on nitrogen fixation (Figure 1). The results are consistent with the literature: Higher temperatures and longer durations lead to a higher degree of curing.

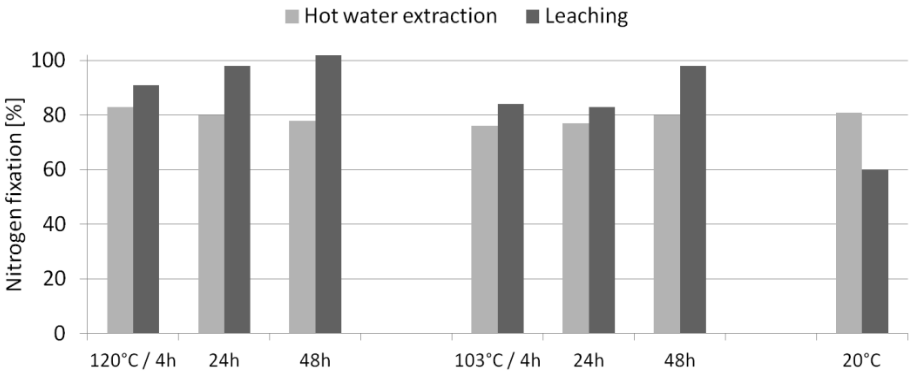

Figure 1: Nitrogen fixation of differently cured and air dried specimen and varied extraction methods

CONCLUSIONS

The N analysis after hot water extraction did not show distinct differences between varying curing conditions or air drying. Based on these results the authors see this method as not being suitable to assess curing quality. In contrast, leaching the samples did show the influence of curing temperatures and durations. This method is adequate and can be seen as a suitable analysis methods for controlling the curing quality of modified wood treated with resin containing nitrogen such as melamine. High fixation rates after leaching ensured proper curing of the samples in the curing variations examined in this study.

For a better understanding of the curing mechanisms, further testing should also include other methods such as formaldehyde emission and -content and work in bending and more curing parameters.

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Field Study in Contact with the Ground of Durability of Thermomodified Scots Pine Sapwood and Poplar Wood and its Chosen Properties

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Keywords: attack, ground, microbes, modification, properties, resistance, wood

ABSTRACT

The scope of use of certain wood species is limited due to the low resistance of wood in weathering conditions and activity of biological factors. Modifying the properties of wood using physical and chemical methods, and the use of wood impregnation with wood preservatives can enhance the natural durability of wood. The thermal modification belongs to methods which may increase performance characteristics of wood, especially in terms of dimensional stability and resistance to water, wood decay or activity of fungi which may cause wood disfiguring and/or wood discoloration. The thermomodification of such wood species as alder, birch, pine or poplar, having rather low natural biologic durability is way for wider application the wood in the building industry among others in the construction of terraces, so also in terms of contact with the ground. The aim of this study was to obtain thermomodified Scots pine sapwood and poplar wood with determining the impact of thermomodification on the physical properties of wood and resistance in ground contact after one year of exposition (as the beginning of the test). The twin samples of both species of the wood were used in the study. The thermally treatment was carried out in an industrial plant, in an open system under conditions of temperature to 210° C, in air saturated by steam. The equilibrium moisture content, density, bending strength and MOE by bending of both wood species decreased as effect of thermomodification, but the compression strength along the grain increased. The results after first year of field exposition, indicate that Scots pine sapwood and black poplar wood slowly decays in ground contact, than the natural wood of these species, showing that thermomodification increased the resistance of wood in contact with ground. The fastest degradation was stated in samples of natural poplar wood.

INTRODUCTION

The exposition of wood to destructive agents, especially weathering, contact with ground or water and condition favourable to growth of fungi and other biological microorganisms damaging wood, may cause rot of wood, changes of wood color, decomposition of chemical constituents, reduction in strength and other properties of wood. It is particularly important for wood species of natural low durability. The scope of their use is certainly smaller than more resistant wood species. The thermomodification is besides of impregnation with wood preservatives a method which may increase performance characteristics of wood, especially in terms of dimensional stability and resistance to water and wood-decaying fungi from the class *Basidiomycetes*. It was however found that the wood is still quite strongly vulnerable to attack of filamentous fungi that cause moulding of wood and soft rot with a prolonged period of favorable conditions for their growth (Fojutowski *et al.* 2009, Militz and Hill 2005). The thermomodification may effect also on some physical properties of wood *e.g.* strength properties. With thermomodification some species of wood as birch, alder or poplar, with low natural biologic durability may however find wider application in particular in the building industry e.g. in the construction of terraces, so also in terms of contact with the ground. Resistance tests of wood determined by field test in ground contact in terms of direct impact of atmospheric and biological factors, are the basis for the assessment of the durability of natural or modified/preserved with biocides wood. Laboratory studies (EN 350-2, EN 599-1), which attempts to mimic the action of biotic and abiotic factors, especially weather, do not play for the full complexity of natural conditions and the effects of their coexistence. The aim of this study was to obtain thermomodified Scots pine sapwood and poplar wood with determining the impact of thermo treatment on the physical properties of wood and resistance in ground contact after one year of exposition (as the beginning of the test). We try to determine the assessment of possibility of extension its use in construction in comparison to Scots pine sapwood. These studies of wood in ground contact are planned to be prolonged to at least five years.

EXPERIMENTAL

To avoid the influence of the heterogeneity of wood on the results of test, twin wood samples were used in the study. 30 twin (directly adjacent to each side measuring 500 × 50 mm) samples, size of 500 (L) × 50 (R) × 25 (T) mm, each of natural and thermally modified black poplar wood (*Populus nigra* L.) or Scots pine (*Pinus sylvestris* L.) sapwood were prepared. The thermally treatment was carried out in an industrial plant, in an open system under conditions of temperature to 210° C, in air saturated steam. The schedule of thermo treatment show Figure 1. The duration of heating in temperature of about 200°C was 3 hours. After heat treatment the wood samples were selected to test (eliminating cracks, warping) and for testing physical properties, small samples adequate to test requirements were cut.

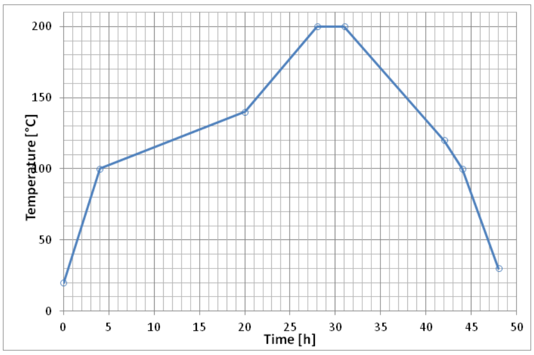

Figure 1: The schedule of thermo treatment of wood

The following physical properties were tested:

- equilibrium moisture content by oven-dry method PN-EN 13183-1, using samples of size 30×20×20mm under standard climate conditions temperature 20°C, relative humidity 65% ; density according to ISO 3131 using samples of size 300×20×20mm (before bending strength tests), bending strength (at three-point bending) according to PN-77-D-04102 (in agree with ISO 3133), samples 300×20×20mm and modulus of

elasticity MOE by bending according to PN-63-D-04117; parallel to grain compression strength (PN-79/D-04102) – samples with dimensions of 30×20×20mm.
Test of wood in ground contact was carried out acc. to EN 252 on field test formed in 2010 by the Wood Technology Institute on Jarocin Forest District lands. The average monthly values of the temperature and precipitation in the observed period showed Fig. 2 (minus 16.0°C was the minimum and plus 33.5°C was the maximum of daily temperatures, yearly mean amounted to +11.2°C; average precipitation in the observed period referenced to days with precipitation was 5.7mm H_2O - daily highest 19.5mmH_2O and smallest 0.5mmH_2O). Rainfall was 385 mm i.e. below long-term average amounting to~ 570 mm.

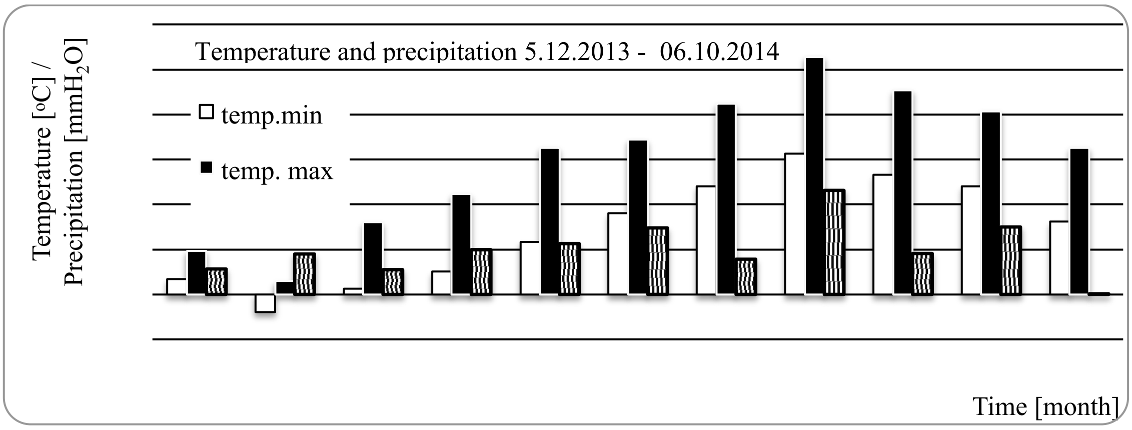

Figure 2: The monthly average temperature and precipitation on field test land

RESULTS AND DISCUSSION

The physical wood properties (Table 1) show that, the equilibrium moisture content, density, bending strength and MOE by bending of both wood species decreased as effect of thermomodification, but the compression strength along the grain increased.

Table 1: Mean values of tested physical properties of wood

Properties	**Scots pine sapwood**		**Black poplar**	
	natural	**thermo**	**natural**	**thermo**
Equilibrium moisture content at 65%, 20°C [%]	12,3	6,9	11,1	4,6
Density at 65%, 20°C [kg/m^3]	540	495	477	422
Compression strength along the grain [N/mm^2]	55,2	64,4	39,3	52,0
Bending strength [N/mm^2]	100,3	83,2	71,5	48,6
MOE [N/mm^2]	10221	9991	6580	6594

The average degree of attack assessment (Table 2) of natural pine wood samples was 1.30 = the state of slightly more than attack known as a light attack (ratingl 1). Softening of the wood does not exceed a depth of 5 mm, and 51% of samples characterized by softening of the wood below a depth of 1 mm. For most samples (63%) showed the presence of white mycelium, and 87% - the presence of mold. The average degree of evaluation samples of thermo-pine sapwood, was smaller=1.17; the presence of hyphae were found in most samples - 60%, while mold occur only on 17% of samples; wood softening was generally less than 1 mm. Poplar wood has been destroyed much stronger - 2.93 degree (PN-EN 252: attack medium - grade 2, and strong - grade 3), including 3 samples were broken, and the depth of softening generally ranged from 8

- 15 mm, indicates the advanced wood decay. The thermo-poplar wood were found poor attack wood, the average degree evaluation of 1.10, the depth of the softening of less than 1 mm in 93% of the samples. Most samples showed the presence of hyphae of natural and modified pine sapwood and poplar wood, while molds occurred mainly on natural wood. There was no occurrence of algae, while on surface of natural poplar wood evidence of gathering microparticles of wood, probably by wasps, was observed. All samples turned greyish, cracks occurred on the foreheads of the samples. With four samples of natural pine wood fruiting bodies of fungi occurred.

Table 2: Assessment of attack caused by microorganisms - 1 year exposition of test stakes - EN 252

Properties	Values	Black poplar		Scots pine sapwood	
		Natural	Thermo	Natural	Thermo
Rating of wood attack	Minimum	2.0	1.0	1.0	1.0
	Mean	2.93	1.10	1.30	1.17
	Maximum	4.0	2.0	2.0	3.0
Depth of wood softening [mm]	Minimum	2	<1	<1	<1
	Maximum	15	3	5	10

CONCLUSIONS

The equilibrium moisture content, density, bending strength and MOE by bending of Scots pine sapwood and black poplar wood decreased as effect of thermomodification, but the compression strength along the grain increased. The thermomodified Scots pine sapwood and black poplar wood after first year of field exposition slowly decomposes in ground contact, than the natural wood of these species and the fastest degraded natural poplar wood.

ACKNOWLEDGEMENTS

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Influence of Wood Species on the Melting Behaviour of Waxes Investigated by Differential Scanning Calorimetry

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Keywords: DSC, melting point, thermal behaviour, wax impregnation, wood

ABSTRACT

For a long time the wood industry has produced wax impregnated wood and wood materials for outdoor applications (*e.g.* Scholz *et al.* 2009). Waxes, oils, and other liquids change thermodynamic properties in porous systems. Due to observations made on wax impregnated wood products, any decrease in the melting point of wax inside wood was investigated. Furthermore, whether or not the wood species used for impregnation has an effect on the melting behaviour of the waxes was analysed. Thus, in the present study differential scanning calorimetry (DSC) was carried out on wax impregnated wood samples to investigate the effect of various wood species on the melting behaviour of waxes impregnated into wood.

INTRODUCTION

Wax impregnation, wherein wax infiltrates wood through vessels and capillaries, is a well-known treatment for wood and wood products made for exterior application. The basic principle of this mechanism is the hydrophobic effect of waxes (Sell 1977). In recent studies, Brischke and Melcher (2015) confirmed an improvement in the long-time durability of wax impregnated wood. A comprehensive description of the permeation mechanisms is given in Scholz *et al.* (2010a, 2010b). Due to distinct structural variation, the impregnability of wood depends considerably on the specific wood species. Difficulties in impregnation often result either from blocked vessels due to the formation of tyloses in hardwoods or from irreversibly closed pits in softwoods.

From studies on various porous materials, the phenomenon of melting point depression is well-known. For example, Jackson and McKenna (1990) performed DSC analysis on meltable materials confined in pore glasses. These authors reported a linear relationship between pore diameter and melting temperature; the smaller the pore diameter the greater the shift in melting temperature. More differentiated physical analyses of the reported behaviour were conducted by Christenson (2001).

Most literature found focusses on the thermodynamic behaviour of substances introduced into inorganic porous structures. However, little is known about the effect of biological materials on the thermodynamic behaviour of meltable substances confined inside the structure. In addition to the known physical effects, the chemical compounds in biological materials, *e.g.* wood extractives, may affect the melting behaviour of the substances introduced. The present work was conducted to study the impact of several wood species on the melting behaviour of waxes.

EXPERIMENTAL

Sample preparation

For the present study, veneers from various wood species were used. The wood species chosen represent a variety of wood extractives, wood extractive contents as well as structural differences (beech (*Fagus sylvatica* L.), fir (*Abies alba* Mill.), heartwood from European oak (*Quercus* spec.) as well as the sapwood and heartwood of Scots pine (*Pinus sylvestris* L.) and larch (*Larix* spec.)).

Before impregnation, the wood veneer samples (*ca*. 10 x 20 mm²) were kiln-dried at 80 °C to constant weight. For impregnation, waxes were melted in an oil bath at temperatures *appr.* 20 °C above their specific melting points. The veneer specimens were immersed in the molten waxes for 15 min. Thereafter, the impregnated samples were covered with an absorbent tissue and briefly laid on a hot plate to remove excess wax from the veneer surface.

Three waxes were used for impregnation (Table 1):

Table 1: Waxes used for impregnation

type of wax	produced by	melting temperature
commercial paraffin	Sasol Wax GmbH	> 100 °C
carnauba wax	Sigma Aldrich	83-86 °C
paraffin wax	Sigma Aldrich	> 65°C

Unmodified veneer samples were used as a reference.

Wax uptake

Wood veneer samples were weighed when absolutely dry and after impregnation to determine the wax uptake as weight percentage gain (WPG) according to Eqn. 1:

$$WPG = \frac{(W_t - W_u)}{W_u} * 100 \qquad (1)$$

where WPG is the weight percentage gain of the sample after impregnation [%], W_t is the weight of the sample after impregnation [g], and W_u is the weight of the absolutely dry sample [g].

DSC measurements

The DSC measurements were performed on a Netzsch DSC 204 F1 Phoenix under a nitrogen atmosphere (flow rate: 50 ml/min). Samples were cut into small squares (*appr.* 7.5 mg) from the impregnated veneer specimens and placed in standard aluminium crucibles with pierced lids. Unmodified veneer and neat waxes with similar weights were used as reference materials.

For the DSC measurements on neat waxes, two heating ramps were applied to the samples. The first ramp was carried out at a heating rate of 10 °C/min from -20 to 20 °C above the specific melting temperature followed by an isothermal segment at the specific final temperature for 10 min. Afterwards, the waxes were cooled down at 10 °C/min to -20 °C in order to obtain good contact between wax and crucible for optimum heat flow. The second ramp at a heating rate of 10 °C/min from -20 to 130 °C was used to determine the melting ranges and peak temperatures.

In contrast, DSC measurements on unmodified and impregnated wood veneer samples comprised only one heating cycle with a heating rate of 10 °C/min from -20 to 130 °C to avoid wax separating from the wood.

RESULTS AND DISCUSSION

DIN EN 350-2:1994-10 estimates the impregnability of various wood species. Pine sapwood (*Pinus sylvestris* L.) is amongst those wood species favourable for impregnation. In contrast, larch (*Larix decidua* Mill.) and spruce (*Picea abies* (L.) H.Karst.) are not as easy to impregnate. Due to the small sample dimensions chosen for the present study, all samples showed good impregnation. ESEM images show wax inside the wood structure and especially inside the cell lumens (Figure 1). Yet, the wax uptake varies significantly (Table 2). The lowest uptake was recorded for pine heartwood impregnated with paraffin wax (WPG = 6 %). In contrast, a high wax uptake was discovered for all wood species impregnated with the commercial wax. Among these, fir (*Abies alba* Mill.) exhibited the most pronounced wax uptake with a WPG of 61%.

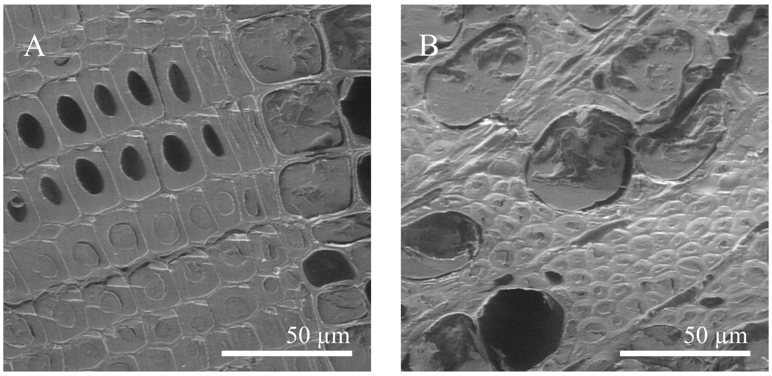

Figure 1: Environmental scanning electron microscopy (ESEM) of samples impregnated with a commercial waxA: Scots pine sapwood (Pinus sylvestris* L.*). B: Beech (Fagus sylvatica* L.*)

Table 2: Results

		carnauba wax		paraffin wax		commercial wax	
		WPG [%]	T_p [°C]	WPG [%]	T_p [°C]	WPG [%]	T_p [°C]
neat wax		100	85.5	100	68.7	100	78.7
fir		44	85.3	32	68.8	61	78.7
larch	hw	15	86.0	15	69.0	26	77.5
	sw	17	84.6	20	69.1	23	79.1
Scots pine	hw	22	83.4	6	68.2	49	78.2
	sw	39	84.7	7	68.1	40	77.2
beech		35	85.0	36	68.9	49	77.1
oak	hw	43	84.7	34	67.8	34	77.4

hw - heartwood, sw - sapwood, T_p *- peak temperature*

During DSC measurements, the samples were heated using a constant heating rate leading to melting of the waxes. For the melting process energy is required, visible in the DSC thermograms of all samples as endothermic peaks. Results are shown in Figure 2 for Scots pine heartwood (*Pinus sylvestris* L.) and European oak (*Quercus* spec.) impregnated with the commercial wax. Whilst unmodified wood did not exhibit any major signals (except for an endothermic peak coincident with the vaporization of water), the treated samples show a major endothermic peak at 77-78 °C. At the same temperature, the DSC thermogram of the neat commercial wax exhibits an intense endothermic peak concomitant with wax melting. Thus, no significant difference was found between melting temperatures of neat commercial wax and wax impregnated to various wood veneers (Table 2).

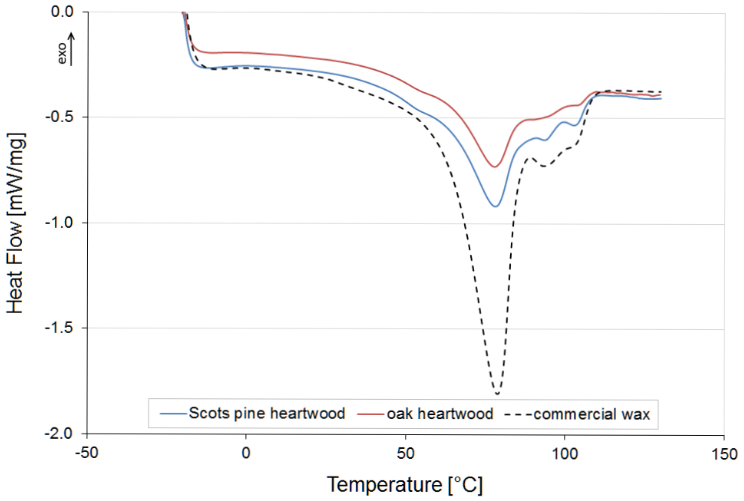

Figure 2: DSC thermogram of Scots pine and oak impregnated with commercial wax and the neat commercial wax. Heating rate: 10 °C/min

Similar behaviour was found for both carnauba and paraffin wax and the corresponding impregnated wood veneer samples. Thus, no assumptions can be drawn concerning the effect of wood structure, pH value, pore size, and extractives on melting point depression in wax impregnated to wood.

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Thermochemical Conversion of Pine and Birch in Slow Pyrolysis

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Keywords: carbon content, carbonization, energy yield, higher heating value, mass yield, slow pyrolysis, torrefaction

ABSTRACT

Slow pyrolysis (carbonization and torrefaction) is a thermochemical conversion whereby biomass is thermally degraded in the absence of oxygen to increase the energy density and fuel properties, such as carbon content (C) and higher heating value (HHV), which is the amount of heat released during the complete combustion of a specified amount of fuel when the water vapour produced is condensed into liquid form. Products of slow pyrolysis are mainly in solid form. In addition to a solid fraction, pyrolysis oil and non-condensable gases are produced from the biomass. The drivers behind the growing consumption and demand for bioenergy are The European Union climate and energy targets for 2020, 2030 and 2050, climate change and the limited supply of fossil fuels. Torrefied wood is promising as a renewable fuel for industrial use due to its grindability, coal-like properties and low ash content. Torrefaction is the early phase of carbonization at temperatures of 200–300 °C. The stemwood of birch (*Betula pubescens*) and pine (*Pinus sylvestris*) including bark (sieve 16 ≤ 8 mm) was pyrolysed at 250, 300, 350, 400 and 450 ˚C to investigate the fuel properties of these tree species. The most remarkable rise of higher heating value (26 MJ/kg) and carbon content (71–72 %) was at 300 °C. At higher temperatures, the increase was minor. The decrease in solid mass yield (46 % and 54 %) was noticeable at 300 °C. Pyrolysed wood reached the higher heating value of coal. Slow pyrolysis increases the higher heating value, carbon content and energy density of torrefied wood and charcoal, but decreases the yield of solid and energy.

INTRODUCTION

The share of renewable energy and primary bioenergy supply is increasing. Bioenergy used more efficiently could make an important contribution to reducing emissions by being a carbon neutral fuel product which neither contributes to nor reduces the amount of carbon in the atmosphere. For example by deploying more efficient conversion technologies, the costs of biomass could become competitive with fossil fuels. The technical and economic challenges of biomass are low bulk density, low calorific value, high moisture content of untreated biomass, thermochemical characteristics and the chemical composition of biomass which complicates the transportation, handling, storage and combustion and increases the costs of biomass for heat and power production compared to fossil fuel equivalents (Eisentraut and Brown 2012). Torrefaction could be one of the conversion methods to overcome these technical and economic challenges. Torrefaction produces mainly a solid fraction but also gases and liquids and differs from carbonization by the lower pyrolysis temperatures (200–300 °C) (Babu 2008, Ciolkosz and Wallace 2011).

The process conditions and raw material have an influence on the pyrolysed end product (Prins *et al.* 2006, Babu 2008). High pyrolysis temperatures reduce the solid yield of char, but increases the higher heating value, carbon content and energy density. Slow pyrolysis reduces moisture and oxygen content and changes the hydrophobic behaviour from hydrophilic to hydrophobic (Pach *et al.* 2002, Yan *et al.* 2009, Cuna Suarez *et al.* 2010). Phanphanich and Mani (2011) reported that the energy consumption of torrefied wood (torrefied at 300 °C) was 10 % of the energy needed for the grinding of untreated wood.

The main objectives of this study were to investigate the impact of torrefaction and carbonization and the altered fuel properties of two tree species of the Northern coniferous forest belt, through this conversion method.

EXPERIMENTAL

Materials and pyrolysis experiment

The raw materials used were the stemwood of Scots pine (*Pinus sylvestris*) and downy birch (*Betula pubescens*) including bark (particle size 16 ≤ 8 mm). The average moisture content of the pre-dried wood chips was 5.3 % (± 0.2).

Pyrolysis was accomplished in a batch-type device using electricity as the external heating method. The heating rate was 20 ˚C/min and the holding time was uncontrolled due to the features of the carbonizing device. Torrefaction pre-tests indicated that nitrogen flow to ensure anoxic conditions was not required. The pyrolysis temperatures were 250, 300, 350, 400 and 450 ˚C. One run at each temperature and raw material combination was carried out. Higher heating value was determined according to the SFS-EN 14918 standard (Solid Biofuels, Determination of calorific value) from samples of 0.5 g (± 0.2), sieve ≤ 1 mm. The bomb process was carried out with a Parr Adiabatic Calorimeter GWB, Model no. 1241EA. Carbon content was determined from ≤ 1 mm samples 0.153 g (±0.09) using an Elementar vario MAX CN-device. The mass of each batch was measured before (M_0) and after pyrolysis (Mt) to calculate the mass yield (n_m) (Eqn. 1) and energy yield (Ey) (Eqn. 2) where HHVt is the higher heating value after pyrolysis and HHV_0 is higher heating value before pyrolysis. The energy density ratio was also determined (Eqn. 3).

$$n_m = Mt/M_0 \tag{1}$$

$$Ey = (n_m * HHVt)/HHV_0 \tag{2}$$

$$\text{Energy density ratio} = Ey/n_m \tag{3}$$

RESULTS AND DISCUSSION

Carbon content, energy yield and energy density

As summarized in Table 1, the results show that the pyrolysis temperature is a significant factor in the slow pyrolysis process. Increasing temperature causes a reduction in energy yield, while the energy density and carbon content increases. Yan *et al.* (2009) showed that according to the results of proximate and ultimate analysis of lolloby pine, torrefaction converts woody biomass from a low energy-density feedstock to a high energy-density feedstock, which may favour wood as a fuel for thermal conversion processes. These results concur with Yan *et al*. (2009) findings.

Table 1. Fuel properties of pyrolysed birch and pine

	Temperature (°C)	**HHV (MJ/kg)**		**Mass yield (%)**	**C (%)**		**Energy yield (%)**	**Energy density ratio**
Birch	untreated	17.3		100.0	47.0			
	250	20.3	(0.5)	77.7	54.9	(0.4)	91.0	1.2
	300	26.1	(0.6)	45.5	71.7	(0.3)	68.5	1.5
	350	26.5	(0.8)	37.9	76.7	(0.4)	58.1	1.5
	400	27.3	(0.8)	35.5	78.9	(0.1)	56.1	1.6
	450	28.2	(0.3)	31.4	81.8	(0.1)	51.1	1.6
Pine	untreated	18.2		100.0	48.3			
	250	20.2	(0.7)	86.0	54.1	(0.3)	95.5	1.1
	300	26.2	(0.6)	53.8	70.5	(1.2)	77.5	1.4
	350	26.8	(0.3)	38.3	76.3	(0.4)	56.4	1.5
	400	27.6	(0.1)	25.6	77.9	(0.3)	38.8	1.5
	450	27.8	(1.4)	32.6	80.8	(0.2)	49.9	1.5

Number enclosed in the parenthesis were standard deviation with n=3

Mass yield and higher heating value

According to Park *et al.* (2010) the most dramatic mass loss occurs during endothermic reactions at temperatures below 300 °C due to cellulose and hemicellulose decomposition. The decomposition of wood is comparable with the findings of Park *et al.* (2010). Half of the initial mass is decomposed at 300 °C (Table 1). Prins *et al.* (2006) reported higher mass loss with hardwoods compared to softwoods. The results are comparable with an earlier study except that at 400 °C the mass yield of pine is 10 percent lower than that of birch (Table 1).

Pyrolysed birch exhibited a higher percentage increase in higher heating values than pine. From the initial 17.3 MJ/kg (birch) and 18.2 MJ/kg (pine) the heating value increased by 63 % and 52 % at 450 °C respectively and reached the values of bituminous coal (Table 1). Phanphanich and Mani (2011) reported the higher heating value of bituminous coal to be 27.7 MJ/kg. Because the density of birch (475–478 kg/m³) is on average greater than that of pine (410–435 kg/m³), the higher heating value of birch is greater per unit volume (Repola 2006). The standard deviation of pine pyrolysed at 450 °C was extremely high (1.4; n=3). This might be due to non-automated sample preparation. The reported higher heating values of pine and birch were slightly higher than earlier studies have shown (Pach *et al.* 2002, Phanphanich and Mani 2011). This might be the result of uncontrolled holding time. The chips were under torrefaction and carbonization conditions for longer which has a positive effect on the higher heating values. Cuna Suarez *et al.* (2010) reported corresponding higher heating values for *Eucalyptus dunnii* of 29.2 MJ/kg, 26.7 MJ/kg and 30.7 MJ/kg at 300 °C, 350 °C and 450 °C respectively, which indicate stabilized heating values temperatures above 300 °C. The results are accordance with previous studies.

CONCLUSIONS

Torrefaction and carbonization increases higher heating value, carbon content and the energy density ratio of woody biomass whereas the mass and energy yield decrease when the pyrolysis temperature increases. At temperatures higher than 300 °C, the increase in carbon and higher heating values stabilize and the mass loss is substantial, which also influences the energy yield and energy density. Pyrolysed wood has favourable properties for applications as a fuel compared to untreated wood.

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Effect of Impregnation with Polymerized Merbau Extractive on Density and Fixation of Compressed Jabon Wood

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Keywords: impregnation, compression, ME, PME, density, set of recovery, Jabon wood

ABSTRACT

A study was carried out with the aim of investigating the effect of impregnation with Merbau Extractive (ME) and two types of Polymerised Merbau Extractive (PME): PME22 and PME33, on the weight gain and density of young plantation Jabon wood *(Anthocephalus cadamba)* followed by combined treatment by impregnation and hot-compression. The compression was done using six levels of pressing temperature, from 120 to 170 °C. A soaking test was conducted to determine the set of recovery of the treated samples. The results of the impregnation with ME and the PMEs showed that the highest weight gain of 31.92% was obtained for the PM33 samples which contributed to the highest density increase of 29.56%. Impregnation with ME did not contribute to weight gain and density increases. Impregnation combined with hot compression contributed to the density increment of Jabon wood and a reduction in the set recovery (SR) of the compressed wood. The best results were obtained for PME33 samples at a compressing temperature of 150 ^{0}C with a density increase of 138.71% and with the lowest SR of 14.82%

INTRODUCTION

Currently, Jabon wood (*Anthocephalus cadamba*) is one of the popular fast growing timber species in Indonesia which is planted widely by both industrial forest plantation companies and by local communities. However, Jabon has not yet complied with the raw material requirements for high quality products (e.g. furniture components or flooring) because of its inferior properties such as lower density and dimensional instability.

Various research studies have shown that the combined wood modification methods of impregnation and compression can improve some desirable properties in timber. Fukuta *et al.* (2011) showed that combined treatment by hot-compression and impregnation by phenolic resin resulted in a product with improved abrasion resistance characteristics, hardness and weathering resistance. Perfect fixation was achieved by Dwianto and Yalinkilic (2000) through a combination treatment on Sugi *(Cryptomeria japonica* D. Don.) sapwood by impregnation using styrene and compression, as well as by impregnation using methyl methacrylate and compression.

This paper presents the experimental results on the effect of impregnation of Jabon wood with merbau extractive (ME) and its polymerization products, polymerised merbau extractives (PME), on the density (D), weight gain (WG) and set recovery (SR) of hot-compressed Jabon wood.

MATERIALS AND METHODS

Preparation of wood samples and impregnating material

The wood used for the experiments was from 5 years old Jabon from West Java, Indonesia. The dimensions of the samples were 50 x 50 x 40 mm [longitudinal (L) x tangential (T) x radial (R)]. Only sapwood was used for the study. The impregnating materials used were: crude merbau extractive (ME) and two selected polymerised merbau extractive solutions (PME22 and PME33) made from ME, resorcinol and formaldehyde.

Impregnation treatment

Impregnation treatment was done in a vacuum-pressure vessel where the vacuum of 0.1 kg/cm^2 was applied to the samples for 30 minutes. The vacuum was then released and the vessel was filled with the liquid of the impregnant, at which point the liquid level was 20 cm higher than the submerged wood samples. Then pressure was applied and maintained at 15 kg/cm^2 for 1 hour. After that, all specimens were placed in a conditioning room until a constant weight was reached. The retention level of the impregnat was determined by calculating weight gain (WG) with the formula as follows (Zaidon *et al.* 2012):

$$WG\% = \frac{W_1 - W_0}{W_0} x100 \tag{1}$$

Where W_1 is the constant weight in a conditioning room after impregnation and W_0 is the constant weight in a conditioning room before impregnation. The density was measured for the samples before and after impregnation.

Hot compression

An open hot-compression press was used in the experiments as shown in Figure. Compression was done on impregnated and non-impregnated samples. The working pressure applied to the samples was 10 kg/cm^2 for 10 minutes in a closed and 10 minutes in an open compression system, with the compression ratio (CR) of 50% as the thickness of the samples was 40 mm. Open compression was undertaken by opening the faucet of moisture releaser (e). The compression process was done at six different levels of temperature from 120 to 170°C with intervals of 10°C. All compressed samples were conditioned in an oven at 100±3 °C until constant weight was obtained and the density after compression was measured.

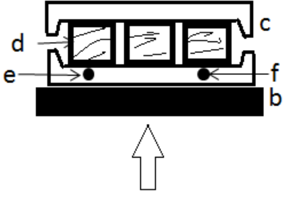


Figure 1: The working principles of hot compression used in the experiment: a = Pressure (Max. 64 MPa); b = hot plate (40 x 40 cm, max 200 ºC) c = removable closed-chamber; d = samples; e = moisture releaser; f = moisture pressure gauge

Soaking test

The samples were soaked in a water bath for 24h, and then drained on a rack in atmospheric conditions for 24h. All samples were conditioned in an oven at 60°C for 3 days before being oven-dried at 100±3°C until constant weight was obtained. The thickness and weight of the samples were measured in the oven dried condition before and after the soaking treatment. The set recovery (SR) effected by water was calculated using the following equation (Dwianto and Yalinkilic 200, Inoue *et a*l. 2008):

$$SR\% = \frac{Tr - Tc}{To - Tc} x100 \qquad (2)$$

where, To and Tc are the thickness in oven-dried (o-d) condition before and after compression, and Tr is the thickness in o-d condition after soaking test.

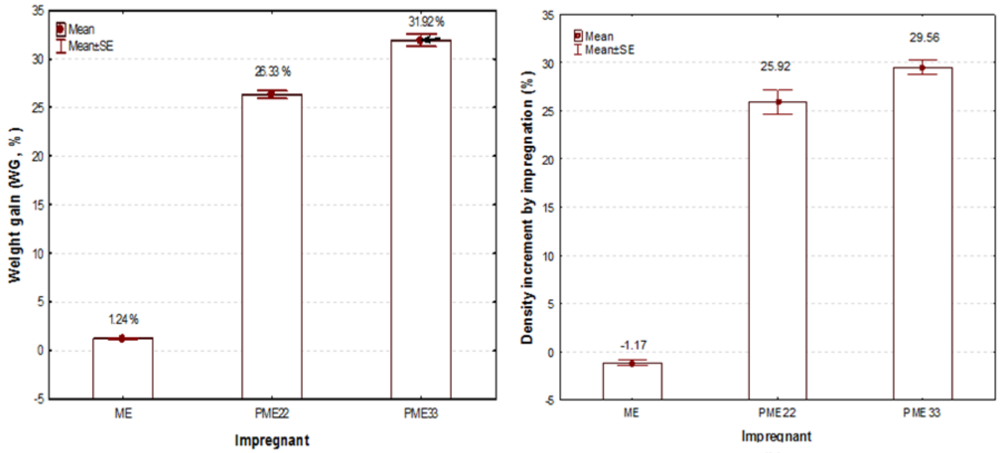
The set recovery (compression set) gives an indication of the elastic recovery of the compressed samples. Low SR corresponds to a better elastic recovery or lower compression set properties.

RESULT AND DISCUSSION

Weight gain and density improvement after impregnation treatment

Figure 2 shows the weight gain and the density increases by the Jabon samples impregnated with ME and PMEs. Statistical analysis shows that the density increment after impregnation using polymerised merbau extractives (PME22 and PME33) resulted in highly significant differences ($p < 0.001$). The highest weight gain of 31.92% was obtained in the PME33 samples which resulted in the highest density increment of 29.56%. Impregnation with ME did not contribute to WG or density increases.

According to Gabriell and Kamke (2010), WG provides an insight into the degree to which the resins are able to penetrate the wood's cellular structure. Higher WGs indicate greater penetration. Yano *et al.* (2001) pointed out that one of the dominant factors in improving the properties and dimensional stability of treated wood is the level of polymer loading.



(a) (b)

Figure 2: Weight polymer gain of Jabon wood after impregnation

Density improvement after combined impregnation and hot compression

Table 1 shows the density increments of Jabon wood following treatment without impregnation, having been impregnated and following a combined treatment by impregnation and hot-compression. The highest density increments after the combined treatment were as follows: at 140°C for the control samples by 58.97%, for ME samples by 58.82% and PME22 by 117.95%, and at 150°C for PME33 samples by 138.71%. Statistical analysis showed highly significant differences ($p < 0.001$) for all variables.

Table 1: Results for density of non-impregnated, impregnated and combined treatment of treatment of impregnation and hot-compressioned of Jabon wood

Treatment		Density increment (%)/ at different Compressing temperature (°C)					
		120	130	140	150	160	170
Non-imp	**Comp**	51.35	48.65	58.97	54.05	58.97	56.41
ME	**Imp**	0.00	0.00	-2.50	-3.03	0.00	0.00
	Imp+Comp	57.14	58.82	57.50	48.48	55.88	58.82
PME22	**Imp**	21.05	21.62	25.64	27.27	25.00	31.43
	Imp+Comp	97.37	110.81	117.95	115.15	107.14	108.57
PME33	**Imp**	25.64	28.95	31.25	32.26	32.43	30.56
	Imp+Comp	117.95	128.95	128.13	138.71	135.14	130.56

Set Recovery

Table 2 shows the set recovery of Jabon wood after performing a soaking test on the samples with combined treatment by impregnation and hot compression. Comparing the control (non-impregnated samples) and the impregnation-treated samples, the lowest SR of 14.82% was obtained for the PME33 samples at a temperature of 150°C, followed by PME22 samples at a temperature of 130°C with a SR of 32.49%. Impregnation using ME only slightly reduced the SR.

Table 2: The set recovery (SR) of Jabon wood after combined treatment

Pre-treatment	Temperature (°C)[a]					
	120	130	140	150	160	170
Control	97.26	97.91	104.87	92.59	104.41	89.84
ME	86.39	82.13	82.69	76.28	72.75	72.52
PME22	48.35	32.49	40.14	41.85	49.15	48.62
PME33	65.85	52.85	37.04	**14.82**	44.45	44.34

CONCLUSION

Impregnation using polymerized merbau extractive combined with hot compression contributes to the density increment of Jabon wood. This treatment also results in a reduction in the set recovery of compressed wood. The best results were obtained for the PME33 treated samples at a compressing temperature of 150 ^{0}C, resulting in a density increase of 138.71% and with the lowest SR of 14.82%.

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Natural Solid Wood Surfaces and Its Possibilities of Using in Health Care and Therapeutic Facilities

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Keywords: antimicrobial effect, health-care facilities, maintenance, plasmatic modification, solid wood surface, wood

ABSTRACT

This paper presents the main advantages of wood in its natural form for the microclimate and its anti-stress impact for users and at the same time its disadvantages in high demand areas. There are three hypotheses that contribute to the statement that wood is suitable for spaces with higher maintenance demands. One is that natural wood, without additional chemical finishing, has natural antibacterial (antimicrobial) features. This paper presents the first tests on the antimicrobial effects of oak and pine wood. Also explored is the antimicrobial properties of wooden surfaces after plasma modification, combining its natural antimicrobial effect with that given by the plasma treatment. The paper presents examples and tests to support these hypotheses.

INTRODUCTION

Natural solid wood is a material with great potential for humanisation of the environment and reaching a state of complex comfort (Majcher 2009), however, particularly in healthcare and wellness facilities, it has disadvantages such as more demanding maintenance to keep the surfaces clean, disinfected and water resistant. To prevent these issues, highly resistant chemical/artificial finishes are used in standard conditions. However, with such chemical finishing many positive effects of the wood on a healthy microclimate are lost.

The goal of this research was to find ideal surfaces for healthcare and therapeutic facilities that retain an authentic visual appearance, have high contact comfort (Teischinger *et al.* 2012, Schönwälder *et al.* 2001) (raw and more rough), that also contribute to acoustic comfort and is antimicrobial/antibacterial and hydrophobic at the same time. In the past, wood has been unfairly classified as an unhygienic material (Stingl and Domig 2011, Schönwälder *et al.* 2001). Up to now, most of the tests dealing with the anti-microbial effects of wood were carried out in the field of food, namely in the contact between wood and the bacteria E-coli and salmonella. However, a study by Milling *et al.* (2005) showed that different wood species displayed completely different hygienic performances. Some wood, especially pine and oak showed excellent antimicrobial characteristics (Matsuda 1996, Forster 1998), efficiently killed bacteria and had clear hygienic advantages compared to other woods and plastics. It has also been concluded that wood surfaces lead to a decrease in the proliferation of inoculated pollutants more than other surfaces, and reduces the survival time of bacteria in wood. This is more evident the higher the amount of pollution and duration.

Antibacterial effect of the low temperature plasma treatment

Low-temperature plasma provides for the multifunctional treatment of wood. In the case of plasma sterilization, the synergistic effects of UV radiation, reactive particles, heat and electric field are present. In recent years, many studies have taken place dealing with the identification of the various components that affect the inactivation of microorganisms. Tino *et al*. (2014) presented an overview of the synergic sterilization effects in atmospheric low-temperature plasma discharge. The main sterilization effects present in plasma are caused by the presence of UV light (Tino *et al.* 2014) (mainly in low pressure plasmas) and mainly due to reactive chemical species present in the atmospheric plasma discharge. Plasma sterilization is a welcome side-benefit in the process of wood activation. A significant reduction in the number of viable microorganisms colonizing the wood structure before the application of a coating system leads to the avoidance, or slowing down, of biological degradation caused by the growth of microorganism colonies (fungi and moulds) underneath the paint film. It is also possible to create nanoscale protective layers in the plasma, which can also contain various biocides.

EXPERIMENTAL PART

Antimicrobial effect of solid wood

Two wood species – pine and oak, each with three different surface finishes – in the raw state with no finish, with a water soluble acrylic lacquer and with an oil-wax natural finish were chosen for the experiment. An overnight inoculum (*Staphylococcus aureus*) was spread over the surface of the pine and oak blocks together with blocks of laminated particle board. The blocks were incubated under the following conditions: room temperature (25°C), relative humidity (40%) and a dark-light cycle. The survival of bacteria was monitored after pressing the blocks against an agar plate and after extraction of bacteria from wooden shavings and swabs after three different times: 0, 5 and 20 hours. The results were quantified by observing the growth intensity of *Staphylococcus aureus* on the agar plate after pressing the blocks from non-wiped blocks and blocks wiped by swabs. Quantification via colony forming units (CFU) was used for counting bacteria that had survived after they had been washed out from the swabs and shavings, respectively.

Antimicrobial effect of plasma treated wood

For testing of the plasma sterilization effect a Kamea Elektron T600 apparatus was used generating an atmospheric low temperature plasma with runaway electrons – ADRE plasma under the following conditions: process gas - N_2, frequency - 2000 Hz, energy of the impulse - 0.6 J, voltage - 312-314V, current - 3A, output - 0.6 kW, plasma treatment times - 30 s, 5 min. Two wood species - sessile oak and pine were used. Two microorganisms *Streptococcus aureus* and *Salmonella enterica* were inoculated on the surfaces of both wood species (wood blocks 7x3x1cm) and their survival after 24 hours and 2 weeks was quantified by counting CFUs on the reference, untreated samples as well as on samples treated for 30 seconds and 5 minutes by ADRE plasma.

RESULTS AND DISCUSSION

Antimicrobial effect of solid wood

On the surface of laminated chipboard a significant amount of live bacteria was found even after 20 hours (Table 1). Comparing the two different wood species, the oak blocks had higher antibacterial activity than the pine blocks. This effect was observed immediately after the application of the inoculum on the wooden blocks. In the second phase the bacteria *Salmonella enterica* was also introduced.

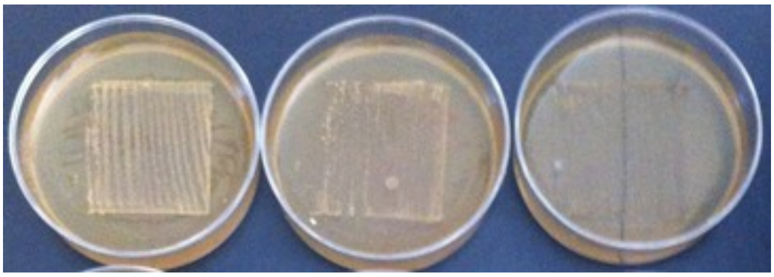

Figure 1: Survival of the bacteria on the surface of pine at 0, 5 and 20 hours, respectively

Table 1: Survival of Staphylococcus aureus on the different surface via log CFU obtained from the swabs after wipe

Blocks	Time	
	0 hour	20 hour
Laminated particle board	7.43	7.11
Pine board	6.56	2.95
Pine board finishing with oil-wax	7.39	6.78
Pine board finishing with acrylic laquer	7.42	7.2
Oak board	3.76	2.34
Oak board finishing with oil-wax	7.41	3.57
Oak board finishing with acrylic laquer	7.32	6.72

Antimicrobial effect of plasma treated wood

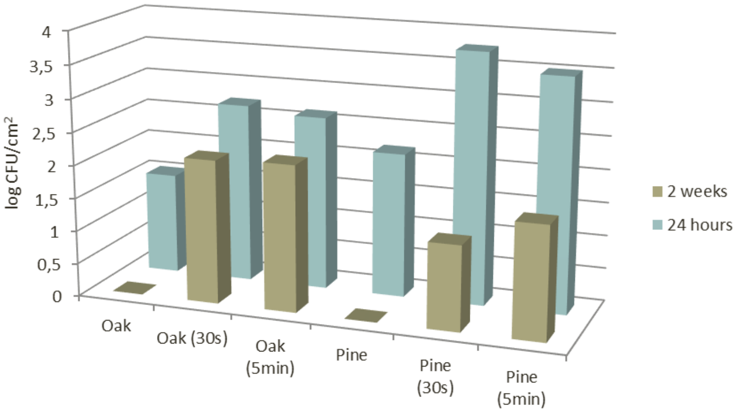

Figure 2: Survival of Staphylococcus aureus on the wood surfaces

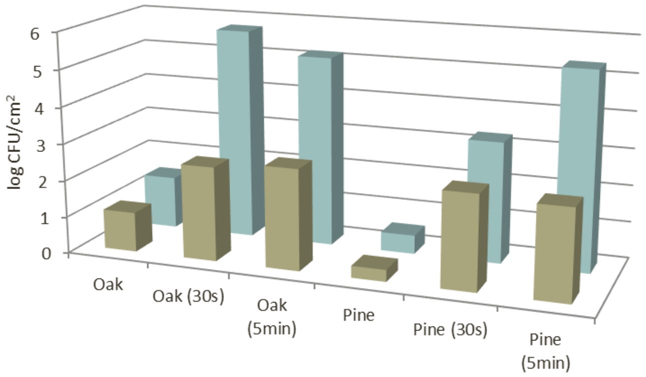

Figure 3: Survival of Salmonella enterrica on the wood surfaces

The reference, plasma untreated samples, proved to have natural antimicrobial properties against the *Streptococcus aureus* microorganism, when samples tested after 2 weeks did not contain any viable colony. However, *Salmonella enterica* seems to be resistant to the extractives of oak wood. From this point of view, pine wood has better antimicrobial properties against salmonella. Plasma treatment (ADRE plasma) in a nitrogen atmosphere lasting 30 seconds and 5 minutes had almost the same effect on the number of viable CFUs of staphylococcus on both woods tested and after 24 hours contained almost twice as much CFUs, as the plasma untreated surface. After 2 weeks the number of viable colonies decreased a bit, but was still higher than on the plasma untreated surface after 24 hours. If the wooden surface was treated by plasma and inoculated after 10 days, the amount of viable bacteria was higher (compared to after 24 hours and 2 weeks respectively). The salmonella microorganism is much more resistant to the plasma treated surfaces of both the woods tested and after two weeks the number of its CFUs were same as those of staphylococcus.

CONCLUSIONS

The use of disinfectants entails the risk of resistant microorganisms. Wood has natural antibacterial properties. A mode of action involves the removal of cells from the surface followed by treatment (removal of water, production of antimicrobial active substances).

Surface treatment – increasing hydrophobicity (through the use of lacquer, oil, plasma treatment) increases the survival of bacteria but makes it possible to use antimicrobial substances.

Plasma sterilizes the wood surface during treatment and immediately afterward, however so far it did not prove to have any long-term sterilizing effect.

ACKNOWLEDGEMENTS

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Wood Modification by In Situ Lactic Acid Polymerization with Tin Octoate– Synthesis and Performance

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Keywords: bio polymers, lactic acid, poly lactic acid, ASE, wood modification

ABSTRACT

Samples of maple were treated with different types of oligomer solutions made from lactic acid. Afterwards in-situ polymerisation of these oligomers was carried out in an oven for different times, at different temperatures and with different catalyst regimes. To characterize the synthesis reaction, DSC and GPC measurements were performed. To determine mechanical and moisture related properties, hardness, MOE, MOR and ASE was tested. The results show that lactic oligomers can penetrate and react to form PLA in the cell wall, leading to permanent swelling. DSC measurements of synthesised PLA showed a great impact of temperature and heating time on the glass transition temperature, whereas the amount of tin (II) 2-ethylhexanoate catalyst, which ranged from 0.5%w to 1.5%w had no significant effect. The mechanical properties and moisture related properties of the modified wood changed due to the treatment.

INTRODUCTION

Wood modification by in situ polymerisation with synthetic resins like phenolic resin, melamine resin or MMA, for example, is well known and some products have been developed (Shams 2004, Rowell 1981). The modification of wood with polymers is not only capable of improving moisture behaviour but it also improves hardness, density and durability. Unfortunately, many of the chemicals used for these modifications are harmful to the environment during use or at the end of the product life cycle. For an eco-friendly modification of wood, non-petroleum, bio-based polymers might have potential in the development of new wood-based products with improved moisture behaviour and durability. The in situ polymerisation of lactic acid in beech and pine wood with different catalyst systems has already been reported (Noel 2009). Results have shown that the polymer properties as well as those of the wood are influenced by the type and the amount of catalyst. Lactic acid polymers can be found inside the cell wall, but no grafting with hydroxyl groups was observed. Due to the biodegradability of wood and the polymer, this modification process seems to be promising regarding environmental concerns. The aim of this study was to determine the influence of reaction temperature, reaction time and pre-polymer processing parameters with different amounts of tin(II) 2-ethylhexanoate as catalyst on the properties of poly lactic acid modified maple (*Acer pseudoplatanus* L.).

EXPERIMENTAL

Material

L(+)-Lactic acid 80 samples (80% aqueous solutions of monomer) were purchased from SysKem Chemie GmbH. Tin (II) 2-ethylhexanoate 92.5-100% was purchased from Sigma. Wood samples with dimensions of 100x20x20 mm³ (L x T x R) were cut from maple (*Acer pseudoplatanus* L.) with an average density of 640 kgm^{-3}.

Pre-polymer synthesis

Two different pre-polymers (PrP) were produced by dehydration of lactic acid in a Heidolph Rotavapor equipped with an oil bath. For PrP1, dehydration started at 500mbar at 95 °C. Pressure was reduced to 60mbar over a time of one hour. Total dehydration lasted 2 hours. For PrP11, dehydration started at 500mbar and 150°C. Pressure was reduced to 100mbar over a time of 3 hours. Total dehydration lasted 4 hours. After that, the pre-polymers obtained were cooled down. For further experiments, Tin (II) 2-ethylhexanoate was used as a catalyst in various amounts (0.5;1;1.5 $\%_W$).

Impregnation

The vacuum (5kPa)-pressure (0.9MPa) impregnation of wood samples with the PrP-catalyst solution was done in a heated (70°C) pressure vessel.

Polymerisation

The PrP-catalyst solutions and also the PrP-catalyst treated wood were further polymerised in an oven at different temperatures with various time regimes.

Molecular weight determination

The relative molecular weights of PrP and polymerised PrP were determined by Knauer GPC with a polystyrol standard. The system was equipped with 3 Agilent PLgel 10 µm MIXED-B columns. Samples were analysed at 40°C. THF as eluent and solvent was used at a flow rate of 1 ml/min and a pressure of 30 kPa. Injection volume was 100µl.

Differential scanning calorimetry

Dynamic DSC measurements on samples with an average weight of 15mg were carried out on a Mettler Toledo DSC 700 at a heating rate of 10k/min. Nitrogen was used as the purge gas with a rate of 20ml/min. Temperature was tested in a range from -50 to 90°C.

Mechanical testing

Samples with two preferable synthesis methods were impregnated and cured (150°C, 3 days curing, 0.5;1% cat./120°C, 7 days curing, 1% cat.). Native samples were treated at the same temperatures and processing times to take account of thermal effects which decrease strength properties (Zauer 2014). Brinell hardness was tested in accordance with ISO 3350. Bending properties (MOE, MOR) were measured according to DIN 52186, sample size was 100x5x5 (LxTxR). Anti-swelling efficiency (ASE) was measured on 20x20x20 mm³ samples which were either stored in 80% humidity or stored in liquid water until equilibrium moisture content was achieved. Afterwards the samples were oven dried. ASE was determined from equation 1 by calculating the swelling coefficient of modified S_m and unmodified sample S_u.

$$\text{ASE}\ (\%) = ((S_u - S_m)/S_u) \times 100 \qquad (1)$$

RESULTS AND DISCUSSION

Polymer synthesis

Glass transition temperature is strongly dependent on the polymerisation time and temperature (Fig. 1). The highest T_g was achieved at 150°C and 3 days polymerisation time. Longer polymerisation at higher temperatures seem capable of further raising the T_g, but the change and decomposition of cell wall material due to the thermal impact would be higher. The amount of catalyst only slightly influences the T_g, but a minimum amount of tin(II) 2-ethylhexanoate is necessary. If the polymer is bound in the wood structure, T_g is increased by 20K compared to the T_g of the pure polymer. Apparently the polymer is reacting in a different way inside the wood structure.

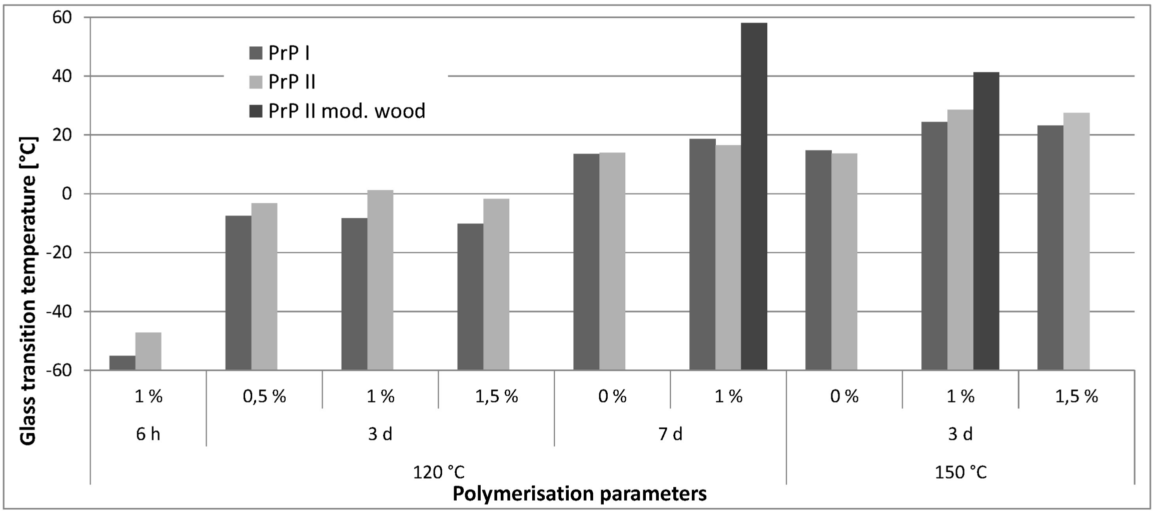

Figure 1: Glass transition temperature of pure polymer and modified wood polymerised with different temperature, time and catalyst regimes

Molecular weight also changes with temperature and polymerisation time. Pure PrP without catalyst has the lowest molecular weight; polymerisation for 3 days at 150°C leads to a polymer with 6282 g/mol. Compared to PLA produced in industrial processes, the molecular weights obtained are fairly low. A better polymer synthesis process may lead to modified wood with polymers more stable in elevated ambient temperatures.

Table 1: Molecular weight of PrP, and pure polymer samples with different temperature, time and catalyst regimes

Sample	M_W [g/mol]	M_n [g/mol]	D_P
PrP II	672	560	1,2
120°C, 1%, 6h PrP II	754	603	1,3
120°C, 1%, 7d PrP II	4155	2409	1,7
150°C, 1,5%, 3d PrP II	6282	3433	1,8

The hardness of modified samples is increased by 320%, but is not affected by higher temperatures or longer treatment times (Fig 2). Since the hardness is strongly dependent on the filled porous volume of the wood samples and the WPG of all variants is about 100%, hardness is not affected by the modification parameters. Modulus of Rupture (MOR) is reduced due to the modification (Fig. 3). Since the PrP has a ph value of 2.5

until the polymer is formed and hardened inside the wood, acid induced decomposition of the cell structure may lead to these reduced MOR values. MOE is not changed. Anti-swelling efficiency is increased due to the poly lactic acid which is located inside the cell wall. After 3 wetting-drying cycles, the ASE amounts to 30-43%, depending on the polymerisation parameters.

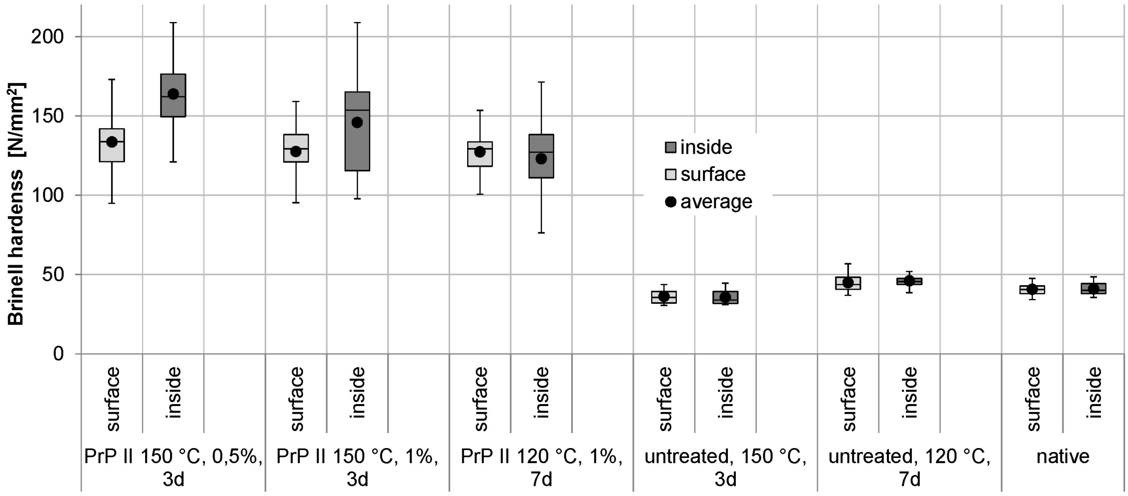

Figure 2: Brinell hardness of polylactic acid modified wood with different temperature, time and catalyst regimes

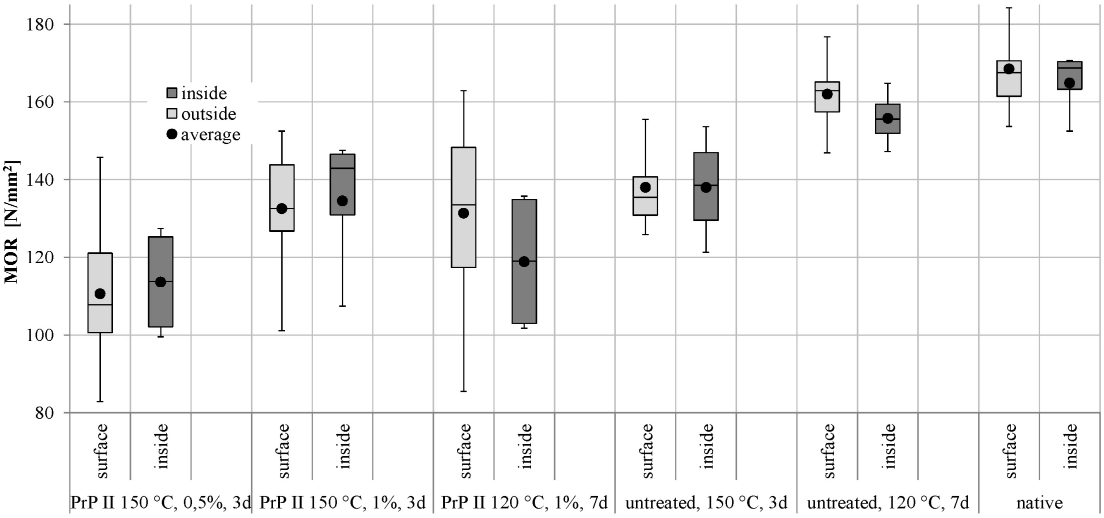

Figure 3: MOR of polylactic acid modified wood with different temperature, time and catalyst regimes

The pH value, measured after each wetting cycle of the modified wood, was about 2.9. This is significantly lower than the pH value of the native wood after each wetting cycle (5.9). Probably some polymer or residual lactic is reacting with water forming lactic acid. Long-term storage for 2 months at 80% relative humidity leads to polymer softening with liquid oligomers pouring out of the samples.

CONCLUSIONS

Synthesis temperature and time have the largest influence on the properties of poly lactic acid modified wood. The amount of tin(II) 2-ethylhexanoate ranging between 0.5 and 1.5% does not affect the synthesis. Dimensional stability is increased by 30% as long as the relative humidity is below 80%. The in situ polymer is not stable for prolonged periods with high humidity. Hardness is increased, but bending strength is reduced. Further investigation is needed to get better synthesis results with a more stable polymer. With better synthesised polymers, this process is a promising new method for wood modification with renewable and recyclable resources.

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SESSION EIGHT

Performance

Monitoring of Window, Door, Decking and Façade Elements Made of Thermally Modified Spruce Wood in Use

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Keywords: colour, heat flux, model house, moisture content, thermally modified wood

ABSTRACT

Thermal modification is one of the most important commercial modification processes. Good performance of thermally modified wood for less exposed applications is known. However, the majority of tests have been performed under laboratory conditions and in standardized field tests. The purpose of the present research was to determine the overall performance of a window, façade and decking elements made of thermally modified and un-modified Norway spruce wood. The observations were performed on model objects at the Department of Wood Science and Technology at the University of Ljubljana. In the period October 2013 to June 2015, temperature, thermal conductivity, blue staining and moisture content were continuously monitored. The results clearly show that the elements made of thermally modified wood have lower thermal conductivity, lower moisture content and are less prone to blue staining. These observations clearly indicate the excellent performance of thermally modified wood in less exposed applications in use class 2 or 3.1.

INTRODUCTION

Thermal modification is one of the most commercially important modification procedures (Esteves and Pereira 2009). The properties of the products depend on the modification temperature and duration of modification (Altgen *et al.* 2012). In spite of the fact that this product has been on the market for almost two decades, the complete mechanism for improved durability has not yet been fully elucidated. The reasons for the increased durability have been assigned to the lower equilibrium moisture content, better dimensional stability, and the formation of new toxic compounds (Hakkou *et al.* 2006). In recent research, another aspect has drawn considerable attention – better moisture performance that is reflected in a lower equilibrium moisture content during exposure.

Thermally modified wood is frequently used in various building applications such as: windows, doors, façades and decking. Wood in these applications is exposed to several biotic and weathering factors. Therefore, the appearance of the wood changes over time and frequently results in unwanted complaints from customers. Hence, it is of great importance to predict changes in thermally modified wood under real conditions and describe possible changes. Another aspect, which is becoming more-and-more important, is the thermal conductivity of materials used in building applications. Windows and doors are mostly made from non-modified wood species, hardly meeting the criteria of the Passive House Institute (Passivhaus Institut, Darmstadt, Germany) without the addition of insulating materials or sophisticated profile design. Recent results indicate that thermally modified wood could be a superior material for the production of energy efficient windows, because thermally modified wood has a thermal conductivity approximately 15% to 30% lower than unmodified wood (Ugovšek *et al.* 2015). Even more, windows made of thermally modified wood have one of the lowest price-performance ratios (Krick 2014).

The aim of this paper was to elucidate the overall performance of thermally modified spruce in building applications and compare it to the performance of untreated Norway spruce wood. Norway spruce was chosen as it is one of the key materials for construction applications in central Europe.

EXPERIMENTAL

The experiment was performed on a window, façade and decking elements made of Norway spruce (spruce) and thermally modified wood Norway spruce (TM spruce). The wood was modified according to Silvaprodukt commercial procedure (Silvapro®) (Rep *et al.* 2004). The temperature of modification was between 220°C and 230°C.

Research was performed on decking, façade and window elements. The cross-section of the façade and decking elements was 2.5 cm × 5.0 cm, the same as prescribed for EN 252 (2012) testing. The length varied between 0.5 m and 1.2 m, depending on the available space. Decking elements were positioned horizontally on the copper treated spruce beams, 0.5 m above the ground in a single layer using steel fasteners. There was 1.5 cm between the elements. The façade elements were fixed on all sides of model house (Figure 1). The model house is located on the field test site of the Department of Wood Science and Technology in Ljubljana (46.048721, 14.479568), approximately 300 m above sea level. The façade and decking were exposed in October 2013. A timber window with a frame width of 68 mm, produced by Slovenian company M SORA d.d., was made of spruce and TM spruce as shown at Figure 1. The window was installed (July 2013) in the test object with a regulated internal temperature of approximately 24 °C as seen in Figure 3.

Figure 1: Test object with decking and façade elements after 18 months exposure and the installed window made of TM spruce (left half side) and spruce (right half side) profile with installed sensors for temperature, moisture and heat flux.

Various types of continuous and non-continuous monitoring were carried out on the wooden material. The façade and decking elements, as well as the window, were equipped with Scanntronik temperature sensors located on the inner and outer surfaces of the profiles. Conductive paste between the sensor and the window enables accurate measurements. From January 2014 to June 2015, all data was collected hourly with Thermofox data loggers (Scanntronik, Germany). Differences between the inner side average daily surface temperatures of the spruce and TM spruce window profiles and the dependence on the average daily outside air temperature were taken into account to analyse the correlation. Heat flux measurements were performed all the time, but data are shown for the period between 25.12.2014 and 6.1.2015, when the lowest temperatures during the whole testing period were recorded. Measurements were performed with four Hukseflux sensors (HFP01) and logged every 5 minutes with a system based on CR1000 (Campbell Scientific, USA).

In parallel, the moisture content (MC) of all the materials investigated was determined as well. MC was determined through resistance measurements. Insulated electrodes (stainless steel screws) were inserted at various positions and linked to a Gigamodule (Scanntronik) that enables wood MC measurements to be made between 6% and 60%. Moisture content was logged twice per day, at midnight and at noon. Weather station Davis is positioned next to the house in order to obtain accurate weather information (temperature, humidity, wind, rain...). On the façade there are custom made sensors that enable monitoring of water condensation and solar radiation. These sensors are positioned on a white plastic surface.

Blue staining was assessed occasionally (Table), according to modified standard EN 152-1 (1996), with marks between 0 (no blue staining) to 4 (75% of the surface is covered with blue staining). Colour was occasionally determined as well. In order to avoid the influence of the moisture on the colour, measurements were always performed after few dry days. Colour was determined with an Erichsen Colour Measuring Device EasyCo 566 and expressed in CIE L*a*b* system. Due to the lack of the space the data of the colour measurements are not presented.

RESULTS AND DISCUSSION

Results on the difference between the temperature on the TM spruce and spruce window profile and their dependence on the outside air temperature are presented in Figure 2. The surface temperature was normally higher in the case of the TM spruce window profile which correlates with the lower thermal conductivity of thermally modified wood. Spruce modified according to Silvapro procedure has a thermal conductivity of 0.09 W/mK, whereas normal spruce has a thermal conductivity of 0.11 W/mK (Ugovšek *et al*. 2015). It can be clearly observed that the difference is drastically influenced by the outside temperature, i.e. the difference between the inside and outside temperatures. As the outside temperature decreases, the difference between the inner surface temperatures is more prominent. When the outside temperature is around 20 °C, the temperature difference is almost negligible.

The difference between TM and ordinary spruce window profiles were also measured using heat flux sensors (Figure 3). It is clearly visible that the heat flux of the TM spruce window profile is lower i.e. the insulation is greater. The difference is most prominent when outside temperatures are low enough (cold days, nights, mornings), whereas the heat flux values of TM spruce and spruce profiles decreased drastically and reversed on afternoons, as direct sun radiation affected the heat flow. In this case, the values of heat flux through the TM spruce profile were higher compared to that of spruce. This is to be expected as the sun was heating up the profiles from the outside. Generally speaking, heat flux values between TM spruce and spruce differed by between 10% and 15%, whereas the measured thermal conductivity of TM spruce is roughly 20% better than the non-modified spruce (NMS). The difference is due to the non-standardized dimensions of the samples – window profiles and boundary conditions have an effect due to the lower width of the measured sample. Once again, differences increased with a decrease in the outside temperatures.

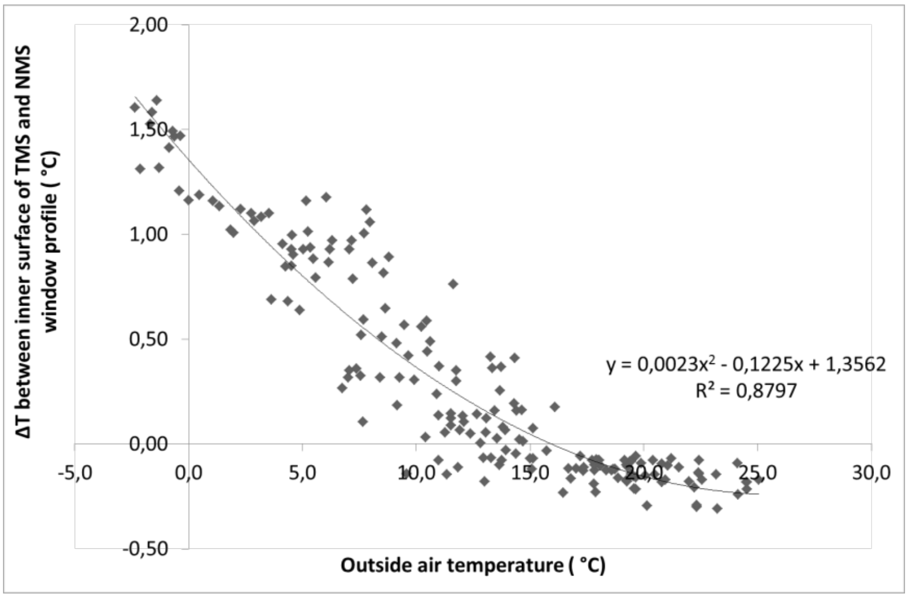

Figure 2: Differences between daily average surface temperatures of TMS and NMS window profile on the inner side of the object in dependence with average daily outside air temperatures

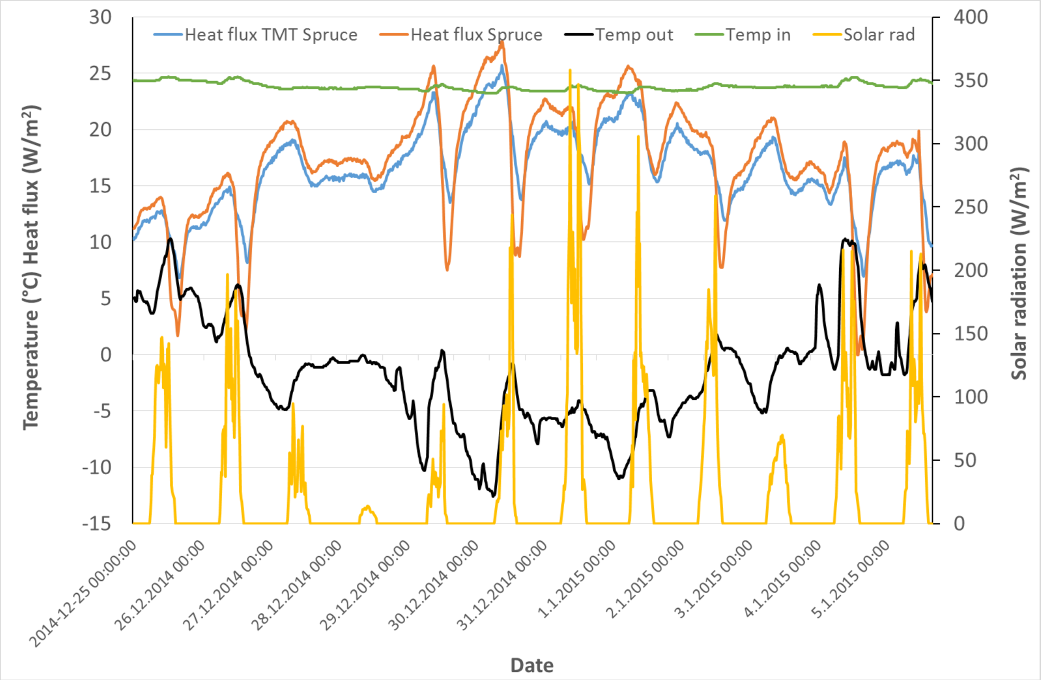

Figure 3: Heat flux through the unmodified and thermally modified Norway spruce wood in relation to outdoor temperature and solar radiation

One of the parameters that influences thermal conductivity is moisture content. As can be seen from Table 1, the moisture content of both TM spruce and untreated spruce remained constant within the monitoring. Thick surface coatings prevent moisture diffusion and capillary water uptake into the window elements. It is presumed that the lower MC of thermally modified wood is one of the factors that contributes to the lower thermally conductivity of TM spruce.

Table 1: MC of Norway spruce and thermally modified spruce wood in the window, façade and decking. Measurements were performed twice per day.

Wood		**Decking**	**Façade north**	**Faç. south**	**Façade west**	**Façade east**	**Window**
Spruce	No of measurem.	850	905	850	1003	770	/
	Average	33.9%	25.2%	24.7%	25.1%	25.8	/
	Mean	33.9%	24.9%	24.6%	24.6%	24.6	/
	U > 20%	850	905	850	1003	770	/
	U > 25%	758	416	336	387	311	/
	U > 30%	587	7	0	46	96	/
	Min	20.2%	20.1%	20.1%	20.0%	20.1	/
	Max	51.5%	47.0%	28.0%	46.2%	48.4	/
	U >20% & t >20	225	241	225	241	241	/
Surface coated spruce	No of measurem.	850	879	643	849	770	935
	Average	27.8%	24.7%	25.9%	28.1%	24.5	9.0%
	Mean	27.0%	24.7%	25.1%	26.6%	24.1	9.0%
	U > 20%	850	879	643	849	770	0
	U > 25%	643	371	334	598	198	0
	U > 30%	250	0	52	262	19	0
	Min	20.1%	20.1%	20.8%	20.2%	20.0	8.2%
	Max	38.6%	28.2%	42.4%	41.2%	36.3	9.8%
	U >20% & t >20	225	218	127	224	241	0
TMT spruce	No of measurem.	849	878	713	658	904	/
	Average	27.6%	13.4%	14.8%	13.4%	13.9	/
	Mean	27.3%	12.9%	13.7%	13.1%	13.5	/
	U > 20%	722	17	121	34	38	/
	U > 25%	548	10	28	9	15	/
	U > 30%	299	4	15	2	10	/
	Min	4.0%	8.5%	3.6%	3.7%	7.1	/
	Max	41.8%	41.6%	35.3%	33.1%	35.2	/
	U >20% & t >20	142	1	15	4	4	/
Surface coated TMT	No of measurem.	/	878	575	658	770	935
	Average	/	12.1%	26.5%	12.4%	15.3	7.0%
	Mean	/	12.1%	26.3%	12.9%	13.7	7.0%
	U > 20%	/	0	467	15	127	0
	U > 25%	/	0	342	7	32	0
	U > 30%	/	0	161	0	19	0
	Min	/	7.4%	4.0%	2.9%	3.6	6.5%
	Max	/	16.8%	41.1%	27.0%	35.3	7.5%
	U >20% & t >20	/	0	115	2	15	0

* *Window was surface coated with thick coating*

Moisture content is, however, of considerable interest from other perspectives as well. Sufficient moisture content and temperature is required for fungal growth and the minimum MC required varies in the literature data. A recent study by Meyer and Brischke (2015) indicates that the minimum MC content varies between 15% and 50%

depending on the wood decay fungi and material investigated. However, most of the optimal values are positioned between 20% and 30%. Optimal values for modified wood were even a bit lower ranging between 16% and 24%.

In order to determine the moisture performance of TM spruce and spruce in different application scenarios, the moisture content of the façade and decking were monitored for between 350 and 500 days. It can be seen from Table 1 that the MC of the spruce wood elements was above 20% during exposure. This was determined on the spruce wood and the surface coated spruce. Only the window that was less exposed to weathering and was coated with a thick coating had a lower MC. On the other hand, the MC of TM spruce was considerably lower. With the exception of decking elements, the MC of the façade elements reached a MC above 20% for between 1 and 7 days only. Surface coating reduced the MC of spruce wood, but was less effective on TM Spruce. The reason for this phenomenon might be the more exposed location of the coated TM spruce elements compared to TM spruce. However, as the measurements are in progress, we will monitor the MC of the façade elements and will see how these elements perform in the future.

Table 2: Influence of the location and surface coating on blue staining of spruce and thermally modified spruce

Wood	Location	Blue staining				
		4 week	10 week	21 week	34 week	54 week
Spruce	decking	1.8	2.5	3.5	x	x
	faç. north	0.2	1.1	2.7	3.2	3.1
	faç. south	0.0	0.0	0.0	0.2	0.2
	façade west	0.0	1.7	2.4	2.7	3.5
	façade east	0.0	1.6	1.9	2.1	2.3
Surface coated spruce	decking	0.0	0.4	0.4	0.5	0.0
	faç. north	0.0	0.0	0.0	0.0	0.0
	faç. south	0.0	0.4	0.4	0.4	0.0
	façade west	0.0	0.7	1.3	1.3	1.3
	façade east	0.0	0.7	0.7	0.3	0.1
TMT spruce	decking	0.0	0.0	0.0	0.0	x
	faç. north	0.0	0.0	0.0	1.7	2.8
	faç. south	0.0	0.4	1.6	1.8	2.0
	façade west	0.0	0.4	0.6	0.9	1.4
	façade east	0.0	0.0	0.0	0.8	1.5
Surface coated TMT	faç. north	0.0	0.0	0.0	0.1	0.8
	faç. south	0.0	0.0	0.0	0.0	0.0
	façade west	0.0	0.6	0.8	1.0	1.0
	façade east	0.0	0.9	1.0	0.7	0.7

x – Blue staining can not be distinguished on grey surface

One of the objectives of this study is to monitor the appearance of decay on the façade and decking elements. As 18 months exposure is not sufficient for the decay to be developed on the decking and particularly the façade elements, we focused on the development of blue stain fungi within the first months of exposure. Blue stain fungi are the reason for the complaints of many customers. As seen from Table 2, the first blue stain fungi appear after the first 4 weeks of exposure, although in November temperatures were rather low. Another obvious result is the fact that blue staining on decking was considerably more obvious than on the façade. However, after 34 or 54 weeks we were not able to fully distinguish blue staining on the weathered surface. Furthermore, a thin layer of acrylic coating that was applied to the tested materials considerably reduces blue staining on all the exposure locations (Table 2).

However, the resistance type moisture measurements on the façade and decking elements have one disadvantage – the MC of the wood is determined in the interior of the samples, at least 1 cm below the surface. Therefore it takes some time after the rain has fallen until the interior of the specimens get wet. Although this method seems very useful for the modelling of decay that predominately starts in the interior of the specimens, this kind of the moisture measurements seem less applicable for the assessment of the influence of the MC on blue staining, that is predominately a surface phenomenon. For example neither the resistance measurements that determine the MC in the interior of the specimens, nor the Davis weather station could determine condensation that appears in the evenings. Therefore, simple water condensation sensors were positioned on each side of the model house to determine how a certain surface is exposed to condensation and how long it takes to dry out. We are aware that plastic and wood can not always be compared, but our method gave us an indication about water condensation in general.

Table 3: Influence of the micro-location on the test building on the time of the wet surface, total daily average solar radiation, maximum and average surface temperature determined on white surface. Measurements were performed between April 2015 and June 2015.

	Faç. north	Faç. south	Façade west	Façade east	Decking
Wet surface [min/day]	444	474	469	723	703
Solar radiation/day [W/m^2]	7644	8164	4495	2585	15432
Max surface temperature [°C]	38.8	40.5	40.5	34.5	44.0
Average surface temperature [°C]	17.6	18.0	17.0	16.9	17.1

The results presented in Table 3 show that the decking is considerably more exposed to wetting as well as to solar radiation. This reflects in the much more prominent greying of the decking, compared to the façade. On the other hand, the façade site least exposed to wetting is the northern façade. This façade is the only façade with an overhang that reduces exposure to the rain. Therefore wood mounted on this façade remained drier, is less grey and less blue fungi developed.

CONCLUSIONS

Model house offers an excellent tool for the assessment of the overall performance of wooden materials and various components. The results from the temperature monitoring clearly indicate that thermally modified wood contributes to the lower heat losses through the windows and enables manufacturers to meet passive criteria. One of the reasons for better thermal performance is the fact, that thermally modified wood has a lower equilibrium moisture content. This can be seen from the lower MC of all elements. Additionally, lower MC contributes to a better resistance to blue staining as well.

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Performance of Thermally Modified Wood During 14 Years Outdoor Exposure

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ABSTRACT

The long-term outdoor performance of thermally modified timber (TMT) from four different industrial heat treatment processes was investigated. Graveyard tests [in-ground exposure, use class (UC) 4] and horizontal double layer tests (above-ground, UC 3.2) with and without artificial shading were performed. Results from field tests after 14 years of exposure were compared with results from short-term laboratory tests with pure cultures of wood-destroying basidiomycetes and terrestrial microcosms (TMC). The thermally modified materials used in the study were: Plato wood (Norway spruce, *Picea abies*, NL), Thermowood (Scots pine, *Pinus sylvestris*, FI), New Option Wood (NOW, Maritime pine, *Pinus maritima*, F), and oil-heat treated (OHT) wood (Scots pine, DE). In addition, Scots pine sapwood and heartwood, Douglas fir (*Pseudotsuga menziesii*), Sessile oak (*Quercus petraea*), and CCB treated Scots pine sapwood (0.7 and 2.8% CCB) were examined as control and reference materials. Based on results from laboratory standard tests with brown and white rot causing basidiomycetes all thermally modified materials were classified as durable to slightly durable [durability class (DC) 2-4]. In TMC tests with unsterile soil against soft rot and other soil-inhabiting micro-organisms all TMT were classified as durable (DC 2). Consequently, all TMT showed remarkably increased durability compared to the untreated controls (DC 5) and reference species (DC 3-5). In contrast, according to the results of the graveyard tests all four TMTs as well as Douglas fir and Sessile oak were classified as less durable (DC 4). Also exposure above ground in horizontal double layers led to a significantly worse durability compared to the one calculated on the basis of the lab test results: Plato, Thermowood, and NOW were classified as 'less durable' (DC 4), OHT performed significantly better. Since not all specimens had failed its durability was preliminarily classified as 'very durable' (DC 1). On the basis of 14 years outdoor testing under different exposure conditions the durability of four industrially produced TMTs turned out to be clearly less than the lab test results indicated. Neither in-ground nor above ground performance met the expectations based on testing with basidiomycete cultures and TMCs. Therefore, short-term durability test methods need improvements regarding their predictive capability for modified wood. In summary, the use of TMT in ground as well as under severe above ground conditions cannot be recommended based on the findings from this field test study.

INTRODUCTION

The heat treatment of wood was one of the first processes aimed at cell wall modification that achieved market relevance and acceptance. Consequently, the first industrially manufactured modified wood products were made from thermally modified timber (TMT) in the late 1990s (Welzbacher 2007). To obtain performance data for this promising, innovative and eco-friendly material as early as possible, this study was initiated in 2001 using very early material from the four important modification processes established at the time in Europe. Comparative durability studies were performed with softwood heat treated according to the Dutch Plato process, the Finnish Thermowood process, the French Retification process, and the German Oil-heat treatment process. Besides laboratory decay tests against brown, white, and soft rot causing fungi, the long-term performance of TMT was studied in the field. On the basis of 14 years outdoor testing under different exposure conditions the durability of the four industrially produced TMT will be discussed.

EXPERIMENTAL

Material

Thermally modified wood from four different industrial processes was tested (Table 1). The various heat treated materials were taken from batches that were produced for the commercial market in the second half of 2000. In addition, Scots pine (*Pinus sylvestris* L.) sapwood was used as a control. Untreated Scots pine heartwood/sapwood, Douglas fir (*Pseudotsuaga menziesii* Franco), Sessile oak (*Quercus petraea* Liebl.) and Scots pine sapwood, vacuum-pressure impregnated in a treatment solution containing 0.7 % and 2.8 % chromium copper boron (CCB) were also tested (Table 1).

Table 1: Materials under test

ID	Wood species	Material	Supplier
Plato	*Picea abies* Karst.	Heat treated, Plato process	Plato Hout BV, NL
Premium	*Pinus sylvestris* L.	Heat treated, Thermowood process	Kestopuu Oy, FIN
NOW	*Pinus maritima* Mill.	Heat treated, Retification process	SA NOW, FR
OHT	*Pinus sylvestris* L.	Heat treated, oil-heat process[1]	Menz Holz, DE
0.7 CCB	*Pinus sylvestris* L.	Pine sap, CCB (6 kg/m³)	BFH, DE
2.8 CCB	*Pinus sylvestris* L.	Pine sap, CCB (17 kg/m³)	BFH, DE
Douglas	*Pseudotsuga menziesii* Franco	Douglas fir	Decker Holz, DE
Oak	*Quercus petraea* Liebl.	Sessile oak	Pfälzische Parkettfabrik, DE
Pine	*Pinus sylvestris* L.	Scots pine	Menz Holz, DE
Pine sap	*Pinus sylvestris* L.	Scots pine sapwood	Menz Holz, DE

Note: CCB = chromium copper boron

[1] *Specimens took up oil during the process*

Laboratory tests

The resistance to wood-destroying basidiomycetes was tested according to EN 113 (1996) using Petri dishes (120 mm diameter) and specimens (n = 12) of 40 x 10 x 10 mm³. The incubation period was 12 weeks. The following strains were used: *Coniophora puteana* (Schum.: Fr.) P. Karsten Ebw. 15, BAM 1/1995; *Poria placenta* var. Monticula (Fr.) Gilbertson et Ryv. FPRL 280, BAM 8/1997; and *Trametes versicolor* (L.: Fr.) Pilat CTB 863A, 1969.

Resistance to soft-rotting micro-fungi was tested in a soil box test (terrestrial microcosm, TMC) according to ENV 807 (1997) using specimens ($n = 20$) of $100 \times 10 \times 5$ mm^3. Natural top soil from the field test site of the Thünen Institute (former BFH), Hamburg, and compost made from horticultural waste was used. Specimens were exposed to soil for 32 weeks.

Relative durability was calculated as the quotient of mass loss of the heat treated, preserved, or natural durable material and Scots pine sapwood controls (x-value, EN 350-1, 1994) as given in Table 2.

Table 2: Durability classes (DC) based on calculated x-values according to EN 350-1 (1994), using results from laboratory tests according to EN 113 (1996) and ENV 807 (1997) and field tests (horizontal double layers) and by adapting the classification according to EN 252 (1989) using durability factors f from field tests instead of the calculated x-values

DC	Definition	Classification based on EN 350-1 (1994) Laboratory tests	Classification based on EN 350-1 (1994) Field tests	Classification adapted to EN 350-1 (1994) – Field tests
1	Very durable	$x \leq 0.15$	$x > 5$	$f > 5$
2	Durable	$0.15 < x \leq 0.30$	$3 < x \leq 5$	$3 < f \leq 5$
3	Moderately durable	$0.30 < x \leq 0.60$	$2 < x \leq 3$	$2 < f \leq 3$
4	Slightly durable	$0.60 < x \leq 0.90$	$1.2 < x \leq 2$	$1.2 < f \leq 2$
5	Not durable	$x > 0.90$	$x \leq 1.2$	$f \leq 1.2$

Field tests

Field tests in soil contact (use class 4, UC 4, EN 335, 2013) and above ground (UC 3) were installed in 2001 in Hamburg-Lohbrügge, Germany, using specimens of $500 \times 50 \times 25$ mm^3 for in ground ($n = 20$) and above ground tests ($n = 10$). The specimens for the graveyard tests in soil contact were exposed in accordance with EN 252 (1989). For determining durability above ground, horizontal double layer tests were exposed with half of the test rigs covered by water permeable textile sheets creating artificial shade as described by Brischke and Rapp (2008).

Decay was assessed annually using the rating scheme according to EN 252 (1989). The ratings were used to determine durability as a relative value between the lifetime of the tested wood and those of a control, *i.e.* Scots pine sapwood. Therefore x-values were calculated according to Eqn. 1. Some materials reached neither the mean nor median lifetime, so durability was calculated as the quotient of the decay rate of the control and the decay rate of the material tested (durability factor f, Eqn. 2). The classification based on either x-values or f-values is shown in Table 2.

$$Durability\ x - value = \frac{Mean\ \ lifetime_{tested\ specimens}}{Mean\ \ lifetime_{control}} \tag{1}$$

$$Durability\ factor\ f = \frac{Deacy\ rate_{control}}{Decay\ rate_{tested\ specimens}} \tag{2}$$

RESULTS AND DISCUSSION

Laboratory test results

The heat treated wood exhibited significantly lower mass loss compared to the untreated Scots pine sapwood controls and some of the natural durable references after exposure to pure basidiomycete cultures (Table 3). However, mass loss strongly differed between

the three test fungi, where *P. placenta* caused the highest mass loss on TMT (*i.e.* 7.4 – 16.0 %), which coincides with previous studies (e. g. Kamdem *et al.* 1999).
More pronounced differences in mass loss were found in soil box tests (Table 3). The mass loss of TMT was in general significantly less compared to the different naturally durable references and controls. Differences between the four TMT were not apparent. Nevertheless, all heat treated materials showed slight attack after 32 weeks of exposure to both, compost and test field soil. As expected, compost soil caused higher mass loss on most of the materials tested, which coincides with previous findings reported by Edlund (1998) and Westin *et al.* (2004).

Table 3: Average mass loss [%] after biological tests according to EN 113 (1996) and ENV 807 (1997) as reported by Welzbacher and Rapp (2007)

Material	*P. placenta*	*T. versicolor*	*C. puteana*	Compost	Field soil
Plato	10.0	6.8	3.7	9.6	4.4
Premium	16.0	9.0	1.9	9.5	5.8
NOW	13.3	7.8	12.2	5.7	4.2
OHT	7.4	5.6	3.4	6.5	4.2
0.7 CCB	16.7	0.5	18.1	3.5	2.6
2.8 CCB	0.4	0.6	0.4	1.0	0.6
Douglas	14.0	2.6	27.4	14.2	12.0
Oak	0.8	14.3	3.9	38.7	39.2
Pine	31.0	5.1	47.5	21.9	21.7
Pine sap	26.2	35.7	60.3	35.6	23.4

Field test results

Most of the materials decayed rapidly when exposed to ground contact (Figure 1). In particular, the untreated control and reference species started to decay immediately, while the thermally modified material decayed more moderately during the first 1-2 years, but caught up in the decay progress afterwards.

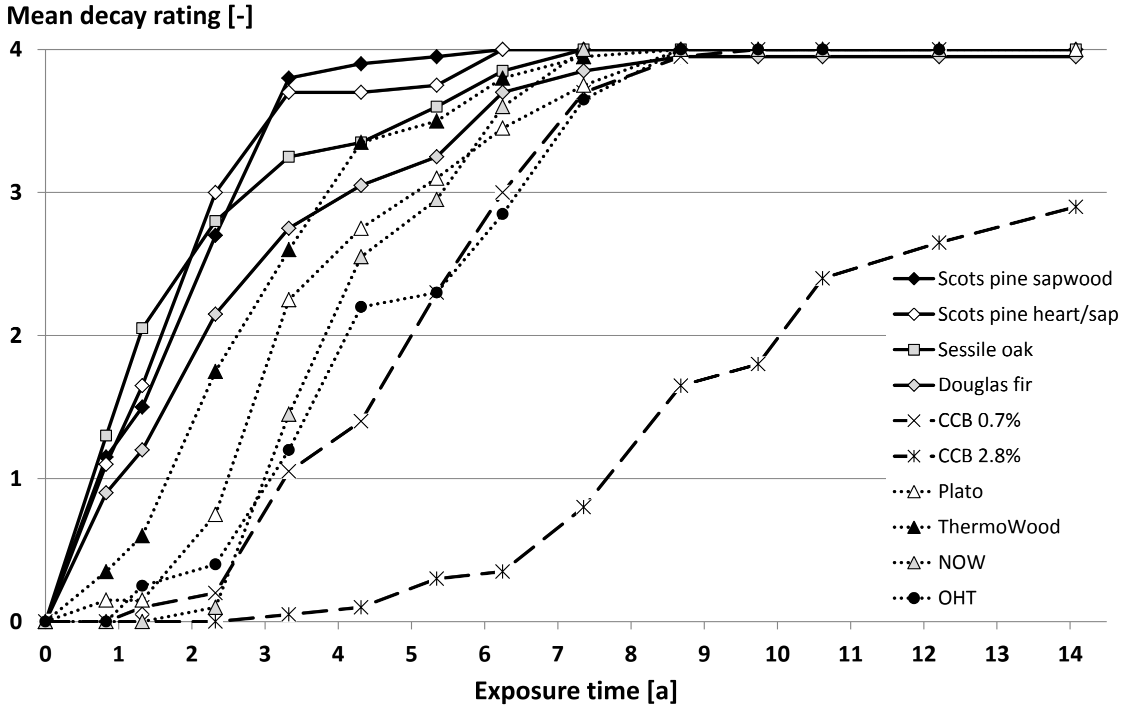

Figure 1: Mean decay rating over time of specimens exposed in ground according to EN 252 (1989)

After approximately 8 years of exposure almost all specimens had failed. Only the CCB (2.8%) treated specimens performed better – they reached a mean decay rating of 2.9 after 14 years. Differences in the decay progress between the different TMTs were marginal, but the performance of the four materials might be ranked as follows: OHT > NOW > Plato > Thermowood. In contrast to the graveyard tests, the above ground horizontal double layer tests exhibited both better TMT performance and clear differences between the materials tested (Figure 2). Furthermore, TMT showed an even more prominent time lag between exposure and the onset of decay in the above ground tests.

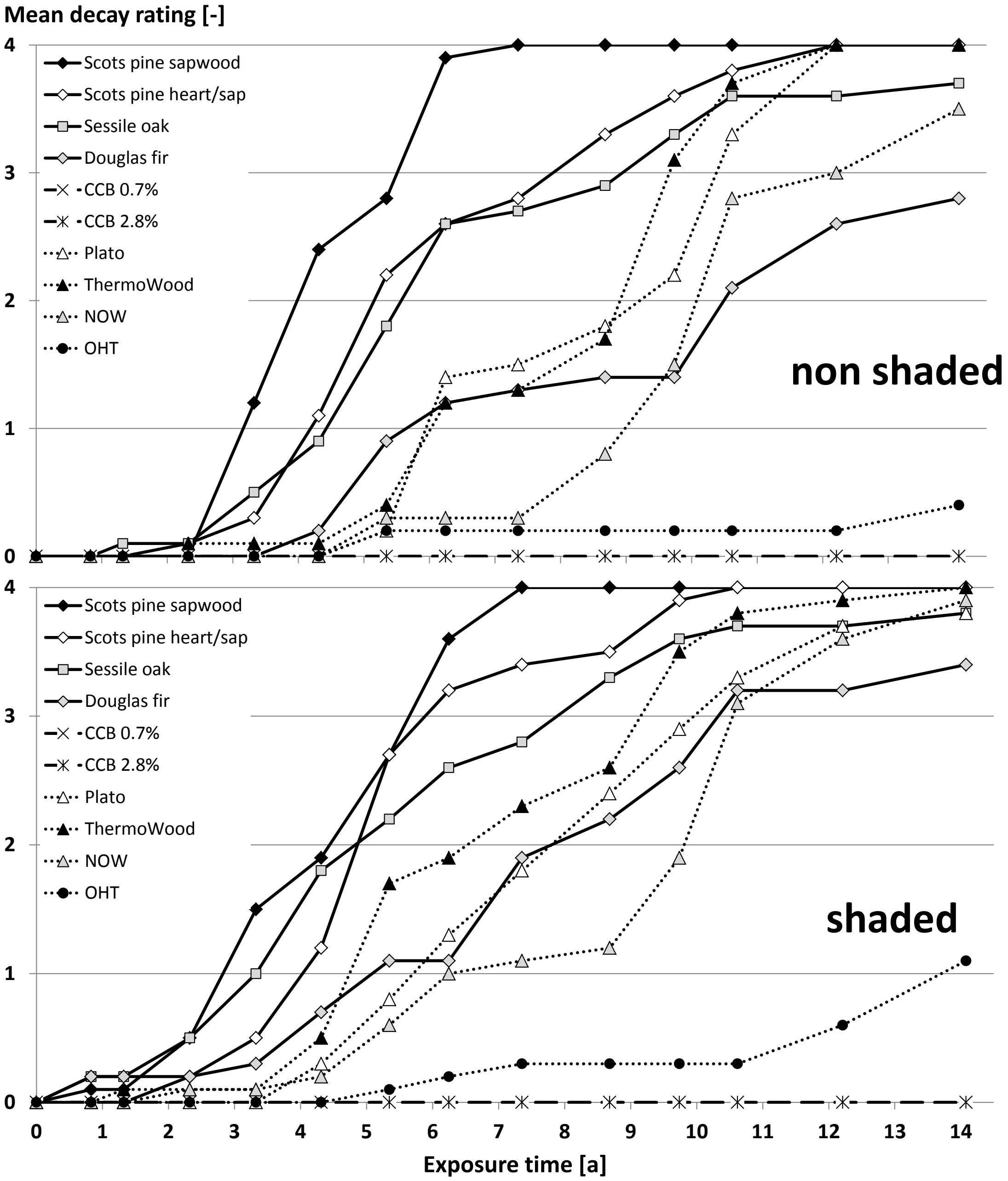

Figure 2: Mean decay rating over time of specimens exposed in horizontal double layers with (bottom) and without shade (top)

Decay proceeded slightly faster in double layers exposed to artificial shade, which stands in contrast to earlier findings by e.g. Clausen and Lindner (2011) and Brischke and Meyer (2015). Besides the CCB treated wood, the OHT material performed well in particular in the shade boxes, where intensive growth of algae was observed (Figure 3). The formation of biofilms may have an inhibiting effect on the growth of decay fungi as suggested by Brischke and Meyer (2015), who found that wood exposed to shade decayed more slowly than wood exposed to sun but receiving the same dosage of moisture and temperature. This seems to become important when decay is provoked by brown rot causing basidiomycetes. However, in this study white and soft rot were the prevailing decay types, as previously reported by Welzbacher and Rapp (2007), which might explain why decay developed faster in the shade.

In contrast to the other TMT, the OHT material exhibited a high oil uptake and thus an oily black surface due to bacterial colonisation. However, below the disfigured surface the wood was light brown, sound and showed only sporadic signs of decay. Consequently, the better performance of OHT might be explained by the hydrophobic effect of the oil shell, even though the samples were not full-cell impregnated, but only cooled in the rapeseed oil bath at the end of the modification process. Similar protective effects of functional biofilms on oil treated wood surfaces were reported by Sailer *et al.* (2010).

Figure 3: Surface of horizontal double layer specimens after 14 years of exposure. Formation of biofilms in artificial shade associated with superficial growth of algae.

Durability classification

Durability classes were calculated based on the different laboratory and field tests and are listed against the specifications given in EN 350-2 (1994) in Table 4. The durability classes obtained differed significantly, depending on the test situation, whereby the most significant deviations were found for the TMT.

In laboratory tests, the durability of TMT was classified as the worst against *P. placenta* as follows: Premium (DC 4), Plato and NOW (DC 3), and OHT (DC 2). Thus, compared with the untreated Scots pine sapwood controls and Scots pine heartwood (both DC 5), durability was significantly increased. The heartwoods of Douglas fir and Sessile oak were classified as being moderately durable (DC 3) and thus in the same range as the TMT. The durability of TMT after exposure to terrestrial microcosms was generally higher compared to the basidiomycete tests. All TMT was found to be durable (DC 2) in both soil substrates, whereas the untreated references were less durable, *i.e.* Douglas fir (DC 3), Sessile oak (DC 5), and Scots pine (DC 5).

Compared to the durability classification obtained with laboratory tests, field exposure led partly to drastic differences in durability. In ground contact all four TMT were classified less durable (DC 4), but also above ground exposure in horizontal double layers led to DC 4 except for OHT, which still performed well and was classified as very durable (DC 1). The untreated references were also classified as less durable (DC 4) in and above ground. Above ground exposure in shade led to worse durability classes in only two cases, *i.e.* for NOW and Douglas fir.

Table 4: Durability classes (DC) based on calculated x-values according to EN 350-1 (1994), using results from laboratory tests according to EN 113 (1996) and ENV 807 (1997), and by adapting the classification according to EN 252 (1989) using durability factors f

Material	*P. placenta*	*T. versicolor*	*C. puteana*	Compost	Field soil	EN 252	HDL shaded	HDL
Plato	3	2	1	2	2	4	4	4
Premium	4	2	1	2	2	4	4	4
NOW	3	2	2	2	2	4	4	3
OHT	2	2	1	2	2	4	1	1
0.7 CCB	4	1	2	1	1	3	1	1
2.8 CCB	1	1	1	1	1	1	1	1
Douglas	3	1	3	3	3	4	4	2
Oak	1	3	1	5	5	4	4	4
Pine	5	1	4	4	5	5	4	4
Pine sap	5	5	5	5	5	5	5	5

The divergence between durability classification based on laboratory and field test results has been previously reported many times (e. g. Junga and Militz 2005, Brischke *et al.* 2009). However, in this study the results from TMC tests clearly overestimated durability in ground contact, and partly also durability in above ground exposure was less than expected. Solely, OHT performed significantly better than could be expected from laboratory test results, which might again be explained by additional moisture protection through an oily outer shell.

CONCLUSIONS

On the basis of 14 years outdoor testing under different exposure conditions the durability of four industrially produced TMTs turned out to be clearly less than lab test results indicated. Neither in-ground nor above ground performance met the expectations based on testing with basidiomycetes and TMCs. Laboratory test methods require further amendments to adequately reflect outdoor field conditions in particular when testing modified wood. In summary, the use of TMT in ground as well as under severe above ground conditions cannot be recommended based on the findings from this study.

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Several Challenges of Wood Modification

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Keywords: acetylation, reaction to fire, regulation of fungi metabolism, water activity, water content.

ABSTRACT

Reduced cell wall moisture content (MC) is accepted by most of wood modification researchers to be the limiting factor for fungal attack. The relative humidity of the environment and the chemical composition and structure of wood determine its equilibrium water content. Not all water in the wood cell wall is accessible to wood destroying organisms. Microorganism cells can metabolize only weakly tied water that has greater chemical potential than water within fungal cell. Otherwise the cell will lose water that could lead to plasmolysis. From the results of water activity measurements on unaffected and decayed wood, culture media and homogenized wood decay fungi mycelium, it is concluded that the water content of wood is not alone the limiting factor for wood decay in moist environments. The cause of reduced moisture content is alterations to the wood composition and structure by modification, beginning at the molecular level. Tightly bound water molecules induce swelling by forming a wood and water solid solution that could make the wood substance more attainable to fungi and facilitate the transportation of decomposed components into the fungal cells. That is the reason why the reduction in modified wood MC correlates with decay retention. Ascertaining the genetic and epigenetic "management" of cell metabolism, modified wood cleavage in absorbable components, their transport into cell for use is the great challenge for wood modification and fungi biochemistry researchers. It needs interaction and cooperation from the both sides. In the distant future a new challenge will emerge in connection with the evolution of decay fungi influenced by their interaction with modified wood. Wood-geopolymer composites (WGPC) were designed and their reaction to fire was tested. Wood-geopolymers composite compositions with silica/alumina ratios from 14.4 to 20.2, timber and minerals ratios from 0.51 to 0.70 as well as sodium silicate fractions in the WGPC from 0.43 to 0.52 correspond with fire resistance to EN A2 class requirements.

INTRODUCTION

Wood is degraded biologically by bacteria, moulds, decay fungi and insects. Most notable is wood degradation by decay fungi and insects (Ibach 2005). Amongst the factors affecting wood biological decay, temperature, oxygen and wood moisture content have a direct impact on the fungus and its ability to metabolize the wood cell wall substance (Viitanen 1997, Brischke *et al*. 2006, Gobakken and Lebow 2010, Viitanen *et al*. 2010). The chemical or thermal modification of wood decreases its hydrophilic properties (Morozovs 2005). Changes in moisture content (MC) and alterations in the wood biopolymers network are to some extent manifested as swelling in case of chemical modification or shrinkage during thermal treatment (Thybring 2013).

Wood MC is frequently used as an input variable to modelling conditions and the resulting risk of decay (Brischke and Thelandersson 2014). Modification of wood with anhydrides lowers the cell wall moisture content in proportion to the WPG attained through acetylation (Papadopoulos and Hill, 2002). The mass percent gain (MPG) of wood by acetylation is used to correlate it with mass loss (ML) in biological decay tests. More than 150 acetylated specimens with different WPG (0-30%) were incubated with *Coniophora puteana* over four months and a 20% WPG threshold was found for wood protection by acetylation against deterioration with this fungi (Švalbe 1978). Rowel (2015) reported a threshold WPG (7-10%) to stop white rot fungal attack and (17-19%) to stop brown-rot fungal attack. Eaton and Hale (1993) suggested that wood is not decayed if it has a MC below 20%. A unified interpretation of wood decay prevention by modification does not exist.

The objective of the paper presented is to survey the results of wood and wood decaying fungi water activity results shown previously (Morozovs *et al*. 2014).

Due to ecological reasons wood is increasingly used in timber constructions. Wood is combustible as is any organic substance. Construction protection against fire is of both major economic and civilian importance. The acetylation and thermal treatment of wood decreases its reaction to fire performance (Morozovs *et al*. 2007, Morozovs and Buksans 2009a, 2009b); a comparison of the fire performance of modified wood with un-treated wood must be performed at equal moisture content, because moisture changes its performance (Buksans and Morozovs 2007).

The objective of presented paper is also an examination of wood-geo-polymer composite (WGPC) reaction to fire and resistance against water exposure with the aim of getting compositions for construction with protection against fire, in an environmentally sound way.

EXPERIMENTAL

The experimental conditions of wood and wood decaying fungi water activity measurements have been presented previously (Morozovs *et al*. 2014). Wood geopolymer composites (WGPC) were prepared from wood cut-shavings, clay and sodium silicate solutions as described below.

Materials: pine wood cutting shavings (with particle dimensions 1.5–2.5 × 3–3.5 × 20–30 mm^3) were from SIA Dendrolight. Clay powder with particle size ≤0.5 mm was from SIA Ceplis and sodium silicate (water glass) solution was from SIA Leana.

Equipment: Memmert forced ventilation oven (Memmert GmbH); Nabertherm muffle furnace (Nabertherm GmbH); stainless steel reactor with electric heating and thermostat (SIA Skutes); conic calorimeter (Fire Testing Technologies Ltd).

Composite specimen preparation: According to the composite composition presented in Table 1, sodium silicate solution was diluted with distilled water and clay powder calcined at 1000 K was added with intensive mixing to for a uniform suspension. Wood shavings were added to this suspension and carefully mixed. The samples with dimensions of 60 × 100 × 100 mm^3 were formed and pressed at a pressure of 8 kPa to a thickness 40 mm over a period of 300 s. Samples were stored in an airtight container in an oven at 338±1 K for one day. After then, the samples were kept in a laboratory for 1 month and finally dried in an oven at 376±1 K until constant mass was obtained.

Reaction to fire tests: Before tests in the conic calorimeter, the WGPC samples were conditioned in accordance with EN 13823:2010 at 296±2 K and RH 50%. The reaction of the sample to fire was rated by: total heat release (THR) [MJ m^{-2}] over 0-300 s, 0-600 s, and 0-1200 s periods; mass loss rate (MLR) [g s^{-1} m^{-2}]; heat release rate (HRR) [kW m^{-2}]; maximum thermal emission rate (MAHRE) [kW m^{-2}]; effective calorific value [MJ kg^{-1}] as well as the total production of carbon dioxide (CO_2) [kg kg^{-1}]. The cone calorimeter heat flux was 50 (kW m^{-2}) with a duration of ≥1200 s.

Table 1: Composition of the wood-geopolymer composite

WGPC composition	Silicon / aluminum ratio (Si/AL)	Wood / minerals ratio (W/M)	Fraction of sodium silicate (NaSi)
GIS1	14.4	0.69	0.43
GIS2	20.2	0.51	0.52
GIS3	15.4	0.73	0.43
GIS4	17.3	0.65	0.47
GIS5	17.0	0.64	0.46

Hydrothermal tests: WGPC samples dried to constant mass were soaked in distilled water for 7 days. Then the samples were boiled in distilled water for one week and subsequently dried at 376±1 K until constant mass was achieved. The water was changed each day during the soaking and boiling tests.

RESULTS AND DISCUSSION

Wood decay and water activity

The wold-wide experience of wood modification assures that acetylation is the best one to provide resistance against wood destroying organisms and give good dimensional stability. Moisture exclusion by modification is supposed to be the mechanism controlling wood decay (Mohebby and Militz 2010, Hill 2006). The blocking of the wood cell wall micro-capillaries with modification reagent has also been suggested as an alternative mechanism of decay prevention by Hill *et al.* (2005). The reason for reduced moisture content is the changes in wood composition and structure at the molecular level imparted by modification and in particular by acetylation (Rowel *et al.* 2009).

Really, the hydroxyl groups in the wood substance (cellulose, hemicelluloses and partly lignin) are assumed to determine water sorption through hydrogen bonds in the wood cell wall (Skaar 1988). Spatially, it is required that the oxygen atom of the hydroxyl group, its hydrogen atom and the oxygen atom of the water molecule are in a straight line in the structure of the hydrogen bond. Both oxygen atoms (in the hydroxyl group and water molecule) have sp^3-electron configuration with the tetragonal lattice of chemical bonds that concede only alone wood hydroxyl group – water molecule hydrogen bond. Willems (2014 and 2015) showed that in an environment with a relative humidity (RH) around 90% each hydroxyl sorption site is tied to a water molecule that conforms to the above.

The water molecule to be linked with wood's hydroxyl group will differ from the ones in bulk water because the hydroxyl group oxygen atom electron density changes due to it interaction with the carbohydrate moiety. Such intermolecular interaction will alter the hydrogen bonds of the first layer of adsorbed water molecules on wood substance in comparison with water molecules in the vapour state.

The fungal cell is able to utilize water molecules that have greater chemical potential than possesses ones inside the fungi. In contrast the cell will lose water that is incompatible with its metabolism. The chemical potential (μ_w) of water is expressed by water activity (α_w) (Eqn. 1).

$$\mu_w = R \cdot T \cdot \ln(\alpha_w) = R \cdot T \cdot \ln(p_s/p_w) \qquad (1)$$

where R is the gas universal constant and T is temperature; p_s is the water vapour pressure above the substrate; p_w is the water vapour pressure above distilled water.

Water activity values decrease in a chain from malt-agar cultivation medium *via* decayed wood to surface mycelium tissue. Wood water activity is equivalent to RH expressed as decimal fraction in the case of equilibrium between wood and environment (Morozovs *et al*. 2014). It means that rot fungi can obtain water from the environment if its tissue water activity is lower than the water activity in the surroundings.

Wood acetylation or thermal treatment does not alter wood equilibrium water activity (Morozovs *et al*. 2014). It could be concluded that water is not the limiting factor for wood decay (Švalbe 1978) though world wide experience with modified wood decay test shows contrary results.

Wood decay fungi need not only water, but also a suitable wood cell wall composition and structure. Moisture exclusion by modification is not the initial intention, but it is an artefact of alterations in the wood cell wall composition and structure. Therefore, the hypothesis that the recognition of nutrients by rot fungi is disrupted, with the subsequent reduction of their growth capacity and expansion, is a more plausible mechanism for wood biological decay prevention (Schwarze and Spycher 2005). Water in the cell wall causes its swelling that facilitates decay and the transport of metabolites into the fungi.

The exact mechanism of wood decay and the biochemical role of all fungal proteins are in general are unknown (Riley *et al*. 2015). Ascertaining the genetic and epigenetic "management" of cell metabolism, modified wood cleavage in absorbable components, their transport into cell for use is the great challenge for wood modification and fungi biochemistry researchers. It needs interaction and cooperation from both sides. In the distant future new challenge will emerge in connection with the evolution of decay fungi influenced by their interaction with modified woods. Such possibilities emerge from the point of view of wood decay fungi evolutionary history (Eastwood *et al*. 2011).

Water activity alone could not be used for the prevention of wood decay but it could be used to investigate the biochemistry of rot fungi.

Results of WGPC reaction to fire

Total heat release (THR) and maximum average heat release (MAHRE) in the cone calorimeter tests of WGPC samples with compositions according Table 1 are presented in Figure 1.

THR decreased inversely with silicon content in the WGPC. A very good negative correlation between THR and (Si/Al) ratio was observed in the first 5 minutes (correlation coefficient -0.98). After 10 minutes it decreased to -0.91, but at 20 minute it was only -0.73, which can be explained by changes in the structure of the WGPC.

The largest contribution to the reduction of THR was given by the mass fraction of the added sodium silicates (NaSi) (correlation coefficients between THR and NaSi were 1.00, 0.84 and 0.61 accordingly). Wood minerals ratio (W/M) increased THR for the test time periods (0-300s, 0-600s, and 0-1200s) with correlation coefficients of 0.98, 0.74 and 0.46 respectively.

Good correlation was observed between WGPC composition indicators (Al/Si, W/M and NaSi) and MAHRE with correlation coefficients of -0.99, 0.87 and -0.95

respectively. Generally, the total heat release (THR) will correlate with MAHRE, but temporarily heat could be released more intensively as a peak of combustion. Heat release rate peaks affected MAHRE more than THR.

Less sodium silicate fraction in the WGPC reinforces its wood fraction exothermic pyrolysis. In addition accelerated wood decomposition in the WGPC increases carbon dioxide yield, which is not desirable, because in the event of fire this would increase the risk of man's suffocation.

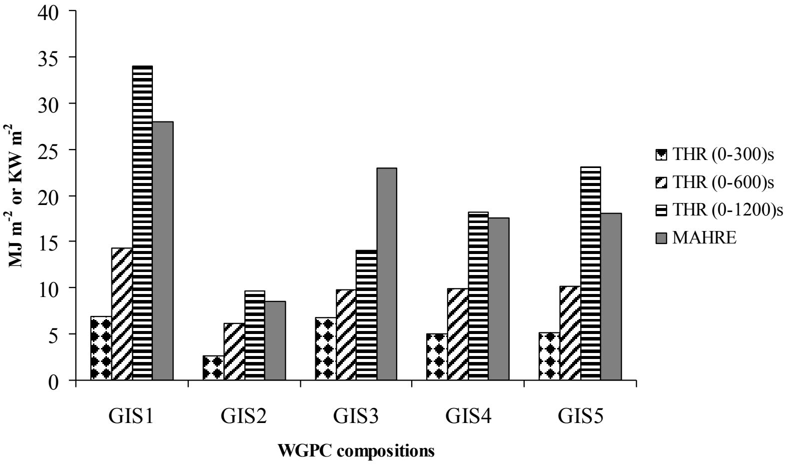

Figure 1: WGPC composition impact on the total heat released (THR) [MJ m^{-2}] during [(0-300) (0-600) and (0-1200)] s during of the test and maximal average heat release (MAHRE) [kW m^{-2}]

The silicon and aluminium sodium silicate ratio in the WGPC closely correlated with the effective heat of combustion (MJ kg^{-1}). Increased silicon content decreased heat release from the composite mass unit during combustion, respectively its correlation with, Si/Al was -0.97 and with NaSi it was 0.93. The increase in the share of wood in the WGPC, of course, increases the heat produced and the correlation coefficient with W/M was 0.86.

The ignition of the WGPC was only observed in the case when W/M was more than 0.7 with the ignition initiated with a spark. It indicates that the minerals and carbon dioxide formed by wood pyrolysis reduces the speed of pyrolysis and the formation of volatile substances that diminish the concentration of flammables, to below those required for sample ignition.

In the case of fire a greater danger for people is smoke, because it disturbs the way of escape. WGPC with lower NaSi and increased W/M had lower smoke emission that could be explained by more complete combustion of the emitted pyrolysis products. The fire performance of all tested WGPC formulations fall under EN reaction to fire class A2.

Geopolymers are characterized by good water and heat resistance. The particles of wood in a WGPC may swell and shrink in changing humidity that could affect the composites durability. The composition of the WGPC were tested against water and heat stresses. After immersion in water, the samples quickly absorbed water, showing good gas and fluid penetration. Water absorption decreased with increasing WGPC mineral content. The maximum water absorbency of the samples reached 100 - 120%. After soaking and boiling, the total mass loss by leaching reached 30±5 %, indicating partial leaching of unreacted sodium silicate. The WGPC samples after the test had an irreversible swelling of 14±3% on average. The results of the hydrothermal tests indicated both the hydrolytic (chemical) and mechanical character of the partial disruption of bonding between wood and the inorganic constituents.

CONCLUSIONS

From a survey of previous results on the water activity measurements of homogenized wood decay fungi mycelium, culture medium, decayed and unaffected wood, the conclusion that wood water content is not alone the limiting factor wood decay in moist environment can be drawn. The cause of reduced moisture content is an alteration in the wood composition and structure at the molecular level induced by modification. The tightly bonded water molecules induce swelling by forming a wood and water solid solution that could provoke better fungi attainability to wood substance and facilitate decomposed components transport into fungi cells. That is reason for modified wood MC reduction negative correlation with decay retention.

Wood and geopolymer composites compositions with silica/alumina ratios from 14.4 to 20.2, timber and minerals ratios from 0.51 to 0.70 together with sodium silicate fractions in the WGPC ranging from 0.43 to 0.52 are available to provide fire resistance according to EN A2 class for constructions. The best fire performance was given by WGPC compositions with higher silicon content. The WGPC tested could be used on the outside parts of constructions as shield, to protect the wood construction against fire.

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Correlation Between Equilibrium Moisture Content and Resistance to Decay by Brown-rot Fungi on Acetylated Wood

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Keywords: Acetylation, acetyl analysis, equilibrium moisture content, decay resistance, dimensional stability

ABSTRACT

There is a direct correlation between the equilibrium moisture content (EMC) and many properties of acetylated wood. This one measurement can be used to predict dimensional stability and fungal resistance.

INTRODUCTION

The number one enemy of wood used outdoors is moisture. Sorption and desorption of moisture results in swelling/shrinking, cracking, coating failure, and surface degradation. Combine moisture with microorganisms and it results in mold growth and decay. Combine moisture with ultraviolet energy and it results in surface erosion, checking and color changes.

As moisture is added to the cell wall, wood volume increases nearly proportionally to the volume of water added (Tiemann 1944, Stamm 1964). Swelling of the wood continues until the cell reaches the fiber saturation point (FSP) and water, beyond the FSP, is free water in the void structure and does not contribute to further swelling. This process is reversible, and wood shrinks as it loses moisture below the FSP. The most hygroscopic cell wall polymers are the hemicelluloses and moisture moves in the cell wall through the hemicelluloses.

Acetylation of wood is a way to change the moisture sorption of the cell wall polymers. The hydroxyl groups of the wood cell wall polymers react with acetic anhydride, resulting in stable, covalently-bonded ester groups (Rowell 2006). For each hydroxyl that is acetylated, there is a mole of acetic acid released as a by-product.

$$\underset{}{\text{WOOD-OH}} + \underset{\text{Acetic Anhydride}}{CH_3C(=O)\text{-}O\text{-}C(=O)\text{-}CH_3} \rightarrow \underset{\text{Acetylated Wood}}{\text{WOOD-O-}C(=O)\text{-}CH_3} + \underset{\text{Acetic Acid}}{CH_3C(=O)\text{-}OH} \qquad (1)$$

All woods contain acetyl groups: softwoods, 0.5 – 1.7% and hardwoods, 2 – 4.5%. Adding acetyl groups in the cell wall results in major changes to the properties and performance of the acetylated wood. In the reaction of wood with acetic anhydride, as the level of acetyl content increases, the equilibrium moisture content (EMC) decreases proportionally (Rowell 2006, Fig. 1). As the level of EMC decreases, dimensional stability increases proportionally (Rowell 1984, Fig. 2). This is logical since the mechanism of dimensional stability is based on bulking of the acetyl groups on the cell wall hydroxyls.

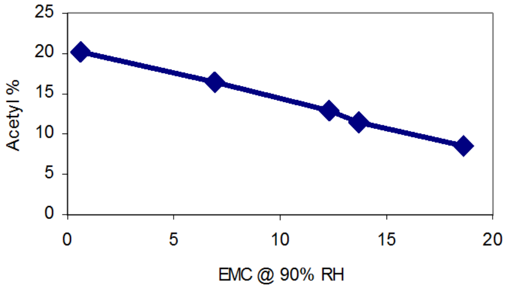

Figure 1: Relationship between EMC and acetyl weight gain

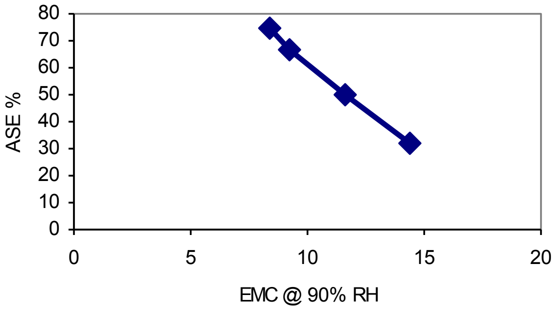

Figure 2: Relationship between EMC and antishrink efficiency

Table 1: Fiber saturation point and equilibrium moisture content of control and acetylated pine

WPG (%)	FSP (%)	EMC 90% RH (%)
0	45	21.7
6	24	17.5
10	16	14.4
18	14	7.2
21	10	4.4

The bonded acetyl groups are less hygroscopic than the unreacted hydroxyls. The EMC of non-reacted wood is 6% at 30% RH, 12% at 65% RH and 22% at 90% RH. Acetylated wood has an EMC of 1.9% at 30% RH, 3.6% at 65% RH and 4.8% at 90% RH. Also, as the acetyl weight goes up, the wood increases in volume. At a level of about 20 percent acetyl weight gain, the volume of the dry acetylated wood is the same as the starting wood green volume.

The relationship between EMC and decay resistance is not linear or proportional (Fig. 3). At an EMC under about 13%, the weight loss due to attack by a brown-rot fungi is less than 5 percent. The reported EMC where no attack occurs is about 8% (Rowell 2006). This data shows that the first hydroxyls to react have the most impact on reducing EMC and increasing decay resistance. It has been shown that the lignin phenolic hydroxyl groups are the first to react with acetic anhydride in wood followed by the hemicelluloses (Rowell *et al.* 1991). The hydroxyls on lignin are almost completely substituted at a weight gain approximately 20 percent acetyl (Rowell *et al.* 1982) while only about 25% of the hydroxyls are substituted on the hemicelluloses.

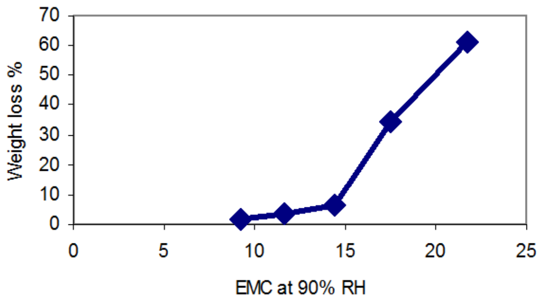

Figure 3: Relationship between EMC and weight loss due to attack by a brown-rot fungus

Based on Figure 1, an EMC of about 13% represents an acetyl weight gain of approximately 12%. The EMC's of the different cell wall polymers at 65% RH and 90% RH are shown in Table 2. At 65% RH, the EMC of the hemicelluloses are close to the level needed to support fungal colonization. Jakes *et al.* (2013) have reported that the glass transition temperature for hemicelluloses at 65% RH is 25°C. This means that at 65% RH, the hemicelluloses are softened and moisture is starting to percolate in the hemicellulose interconnecting matrix. At 90% RH, the EMC in the hemicelluloses is well over the moisture level needed for fungal colonization. The glass transition temperature for dry lignin is approximately 135°C and wet 60-90°C.

Table 2: EMC of cell wall polymers at 65% RH and 90% RH

Cell wall polymer	EMC @ 65% RH	EMC@ 90% RH
Hemicellulose	22	38
Lignin	7	16
Wood	11	21
Cellulose	5	12

Figure 4 shows electron micrographs of pine control before test and acetylated after a 12 week ASTM standard test using a brown-rot fungus. Note that there is a hypha (arrow) on the radial wall and it is growing on the S_3 layer. Maybe we need to know more about the S_3 layer chemistry.

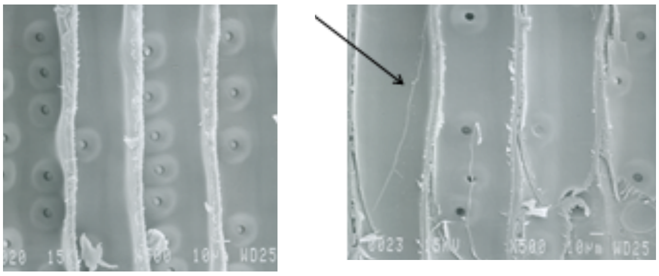

Figure 4: Electron micrographs of pine control before test (left) and acetylated after 12 weeks with a brown-rot fungus

While brown-rot fungi as a whole only represent about 6% of the total fungi in the world. Their attack results in strength loss and massive weight loss mainly in softwoods. There are many theories on the mechanism of the attack of brown-rot fungi on softwoods. Many researchers have tried to explain the mechanism as being one or two steps. However, I think that is too simple and the actual mechanism involves many steps as I theorize as follows:

Step 1 – A favorable environment

Fungi need an environment that is conducive to their survival: temperature, moisture, pH, and toxicity. If the temperature is too high or too low, the fungi cannot survive. If the wood is too wet or too dry, the fungi cannot survive. If the pH is too high or too low, the fungi cannot survive. And, if there are toxic chemicals in the wood, the fungi cannot survive. If the environment is favorable, then the degradation mechanism progresses to Step 2. Resistance to attack by acetylation might function at this level with a moisture content too low for colonization (Rowell 2012).

Step 2 – Recognition

The pH of the wood starts to drop as the fungus starts to colonize. The hyphae of a brown-rot fungus must detect a source of nutrition in the wood it has come into contact with in order to survive. The first attack is thought to be in an oxidation and rearrangement of lignin by an enzymatic reaction. No lignin is lost but it is known to be somewhat oxidized and condensed. If the colonization takes place, then the mechanism progresses to Step 3. At this stage, the fungus is undergoing gene expression to start the production of cellulosic enzymes (Alfredsen *et al.* 2015, Ringwood *et al.* 2014). It is possible that the fungal enzymes cannot recognize the modified cell wall polymer substrates since this enzyme reaction is very specific.

Step 3 – First attack

Since the result of brown-rot degradation is mainly a loss of cell wall carbohydrate polymers, it is logical to assume the first degrading reaction is an enzymatic attack on some very easily hydrolysable carbohydrate sugar that is probably located in the side chain of an accessible hemicellulose structure. The hypha grows in the inside of a cell wall so it is in contact with the S3 layer which is rich in hemicelluloses. The products of this attack provide the energy to proceed to a major chemical reaction in Step 4.

Step 4 – Fenton chemistry

The first enzyme reaction then leads to the generation of a peroxide/ferrous ion and a hydroxyl radical chemical system (Fenton 1894) that depolymerizes the structural polysaccharides in the cell wall matrix resulting in strength losses (Goodell 2006). The hemicelluloses and the cellulose polymers start to degrade and major strength losses are observed.

Step 5 – Weight loss

As this Fenton chemistry progresses, new enzyme reactions take place in other accessible regions of the cell wall polysaccharides resulting in significant weight losses. Very little lignin is lost in the final stages of attack.

Acetylation of wood may be effective in resisting attack by brown-rot fungi by creating a hostile environment with a very low cell wall moisture content (step 1). It may also be that the change in the substrate-enzyme specific reactions can not take place in step 2 (recognition). It also might be the modification of the lignin that inhibits the oxidation and condensation of the lignin in Step 3. Or, it may be combination of these and many other factors.

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The Water Glass Technology: Improving Wood Resistance against Subterranean Termites and Decay Fungi by the Mineralization Process

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Keywords: decay and termite resistance, moisture uptake, wood mineralization

ABSTRACT

The mineralization process initially developed for the hydrophobation of stone and concrete was applied to wood with the aim of conferring new properties in terms of hydrophobation, dimensional stability, mechanical resistance and protection against wood destroying organisms. Laboratory durability tests were performed in order to estimate the preventive efficiency of two products with high silica content, applied to wood by deep impregnation, against *Reticulitermes* subterranean termites and basidiomycete decay fungi, according to an adaptation of the European standards EN 117, EN 113 and CEN TS 15083-1. Additionally, immersion tests were done to determine the water uptake of the mineralized wood samples. Both products decreased water uptake and improved wood resistance against both subterranean termites and decay fungi. However, different moisture uptakes and release kinetics and different types of damage were recorded depending on whether the impregnated wood species was beech or Scots pine, highlighting the impact of wood anatomy on the potential protective efficacy of the test products.

INTRODUCTION

The process of mineralization, defined as the incorporation of liquid glass in a given material, has been used for many years for the hydrophobation of stone and concrete. The treatment, consisting of spraying liquid formulations with high silica contents on the surface of the material to be protected, does not lead to aesthetic modification of the material and allows a progressive filling of its natural porosity. The integration of silica modifies the surface properties of the treated material and generates irreversible chemical reactions. This type of treatment, little sensitive to UV radiation, allows an application to be sustained without the necessity for particular renovation.

Treatments based on inorganic chemistry constitute innovative alternatives to traditional wood preservation. Several products exist in Europe for the preventive or remedial treatment of wood for indoor use (Nahos ®, HDK ® N20, Wood Bliss ®, Termibio ®) but they remain very marginal. The mineralization process, consisting of soaking wooden chips with a mineral solution, has been used to improve the long-term stability, as well as the reinforcement, of lightweight concrete made of wooden wastes (Courard *et al*. 2011, Corinaldesi 2012). In North America, the TimberSil ® Glass Fusion process is regarded as a non-toxic and effective fire retardant, a barrier against insects and is guaranteed not to rot or decay for 40 years.

Many authors (e.g. Furuno *et al.* 1991, Furuno *et al.* 1993, Saka *et al.* 1997, Yamaguchi 1994, Yamaguchi 1994) have carried out studies based on many inorganic compounds to improve the performance of wood (biocide action, fire resistance, etc.). Many silicone-based treatments, using various compounds (silico-fluorides, colloidal silicic acid solutions combined with various metal compounds or boric acid) have been tested with regard of their ability to act as preservatives or biocides; they have shown good performance. Water glasses have also been demonstrated to enhance the durability of wood (Mai *et al.* 2004, Yamaguchi, 2002).

The objective of the research presented in this paper was to study the possibilities of transferring the mineralization process developed for concrete and stone to wood, with the aim of providing new properties in terms of hydrophobation and protection against wood destroying organisms (insects and fungi).

EXPERIMENTAL

Determination of the long-term water uptake of mineralized wood

Scots pine (*Pinus sylvestris*) and beech (*Fagus sylvatica*) blocks of 50 mm x 25 mm x 15mm were impregnated under vacuum (at 1 Pa for 15 min) with two different products with high silicate content, called mineralizers HM1 (ethanol based) and HM2 (water based). The treated wood specimens were weighed immediately afterwards and again after reaching constant mass (equilibrium was reached after 2 to 4 weeks at room temperature).

In order to study their water absorption and desorption rates, the mineralized wood samples were fully immersed in a bath of demineralized water at room temperature (20±5°C), along with untreated specimens used as control samples and were maintained in the submerged state for 28 days. Water uptake was assessed by weighing the samples after 1, 2, 4 and 8 hours, and then, after 1, 2, 4, 8, 10, 14, 21 and 28 days. Finally, the samples were removed from the bath and placed on a grid for 8 days at room temperature to allow desorption. Measurement of variations in sample weight were performed after 1, 2, 4, 8 hours and 1, 2, 3, 4, 7, 8 days.

10 replicates were used for each test product/wood species. Additionally, 10 specimens of untreated Scots pine and beech were used as controls.

Determination of the resistance of mineralized wood against fungal decay

The resistance of Scots pine specimens treated with HM1 and HM2 against basidiomycete fungi was assessed using a test protocol adapted from the two European standards EN 113 (1997) and CEN/TS 15083-1 (2006).

The test specimens were dried, impregnated under vacuum with HM1 and HM2 and conditioned prior to testing at 65% RH and 22 °C, until constant weight was reached. Then, they were exposed to the Basidiomycete fungi *Coniophora puteana* (CP) and *Poria placenta* (PP). Two specimens, one treated and one untreated were placed together in each test device. 10 specimens were used for each test product and each species of fungus, and 10 samples of untreated Scots pine were used as virulence controls. After 16 weeks exposure, the specimens were cleaned, dried and their mass loss due to fungal degradation was determined.

Additionally, 10 samples were treated with each product, allowed to stabilize, and dried in order to determine the dry mass of mineralizer retained by the wood samples. The mean dry mass calculated was used to determine the correction factor to be applied to the test specimens. Indeed, because samples exposed to fungi were initially dried before being mineralized and not after the treatment, the final calculation of their mass loss needs to take into account the weight of silicates impregnated into wood.

Because the mineralizers HM1 and HM2 are believed to be non-biocidal products, the resistance of the impregnated samples was evaluated based on the natural durability classification against Basidiomycete fungi, as described in the standard EN 350-1 (1996).

Determination of the resistance of mineralized wood against subterranean termites

The resistance of wood mineralized with HM1 and HM2 was determined using a test protocol adapted from the standard EN 117 (2005).
5 specimens of Scots pine sapwood were impregnated with HM1 and 5 with HM2. Additionally, 3 specimens of beech were impregnated with HM2. 3 untreated Scots pine specimens were used as controls. All samples were individually placed in contact with 250 *Reticulitermes flavipes* termites. All test devices were then placed in an air conditioned testing chamber, with the temperature controlled at 22 (± 2) °C and relative humidity of 70 (± 5) %. The total duration of the test was 8 weeks.
At the end of the test, the survival rate of termites was recorded and a visual examination of each test specimen was carried out. Any evidence of attack was expressed as described in Table 1.

Table 1: Principles of evaluation of termite attacks on wood according to EN 117

rating	**level of attack**	**description**
0	no attack	
1	attempted attack	• superficial erosion of insufficient depth to be measured on an unlimited area of the test specimen • attack to a depth of 0,5 mm if restricted to an area or areas of max 30 mm^2 in total • combination of both
2	slight attack	• erosion of 1 mm in depth limited to max 1/10 of the surface area of the test specimen • single tunnelling to a depth of up to 3 mm • combination of both
3	average attack	• erosion of <1 mm in depth over more than 1/10 of the surface area of the test specimen • erosion of >1 mm to <3 mm in depth limited to max 1/10 of the surface area of the test specimen • isolated tunnelling of a depth >3 mm not enlarging to form cavities • any combination
4	strong attack	• erosion of >1 mm to <3 mm in depth of max 1/10 of the surface area of the test specimen • tunnelling penetrating to a depth >3 mm and enlarging to form a cavity in the test specimen • combination of both

RESULTS AND DISCUSSION

Measurement of the retention of the test products in wood

Prior to water uptake and biological testing, all the treated wood specimens were weighed in order to determine the retention of the silicate-based solutions in wood. Weight percent gain (WPG%) was calculated according to Eqn. 1.

$$WPG\% = (Ww - Wd)/Wd * 100 \qquad (1)$$

Ww = “wet weight”, which is the weight measured after wood specimens reached constant mass
Wd = “dry weight”, which was calculated by oven-drying wood specimens prior to impregnation

The WPG calculated for Scots pine and beech with both HM1 and HM2 mineralizers are shown in Table 2. Each value reported in the table is the mean of 40 individual values.

Table 2: Weight Percent Gain (WPG) of mineralized wood specimens

Mineralizing product	**Wood species**	**Mean WPG (standard deviation)**
HM1	Scots pine	61.5% (8.9%)
	Beech	14.3% (1.2%)
HM2	Scots pine	19.5% (1.6%)
	Beech	43.7% (4.3%)

The ability of Scots pine and beech to be impregnated with the test products appeared very different, depending both on the wood species and the product used. HM1 achieved a better impregnation in Scots pine, while higher retention levels were reached in beech with HM2.

Determination of the long-term water uptake of mineralized wood

Water uptake measurement is an easy way to estimate the hydrophobic effect of a product impregnated into wood or applied on the wood surface (Dalton 1994, Jiang and Walker 2007).
The percentage water uptake (WU) is measured using equation Eqn. 2:

$$WU\ (\%) = (Wt - Wi)/Wi * 100 \qquad (2)$$

Wt = weight measured at each time interval
Wi = initial weight (t=0)

Figure 1 shows the water-uptake profiles, based on the weight percentage gain, of wood specimens treated with the two mineralizers, on a total time scale of 28 days.

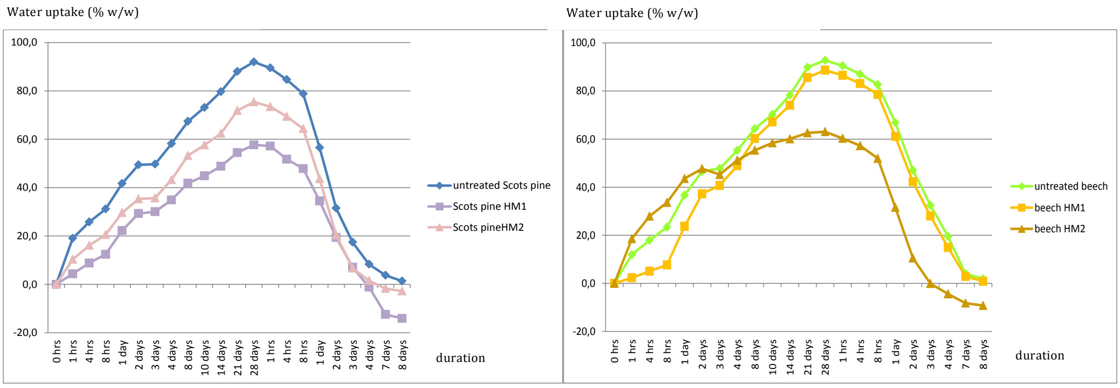

Figure 1: Water uptake (% m/m) of Scots pine and beech samples untreated and impregnated with mineralizers HM1 and HM2

The results showed that both mineralizers reduced water uptake into impregnated Scots pine specimens, HM1 being the most efficient (mean WUs after 28 days: untreated Scots pine = 91.9%; treated with HM2 = 75.4%; treated with HM1 = 57.7%). Conversely, water uptake into impregnated beech specimens mineralized with HM2 was reduced, while the behavior of specimens mineralized with HM1 was similar to the untreated ones (mean WUs after 28 days: untreated beech = 92.7%; treated with HM1 = 88.6%; treated with HM2 = 63.0%). These observations are consistent with the WPG of the wood specimens measured after impregnation with the two tested products; the highest retentions leading to the lowest water uptake percentages.

Similar studies were performed on wood specimens treated with different hydrophobers such as silicones (Simon *et al.* 2011, Malassenet *et al.* 2014, Lhumeau *et al.* 2015). Compared to the untreated samples, water-uptake reductions after 28 days in the Scots pine specimens treated with different silicone-based products ranged from about 10% up to 60% in the most favorable cases. In the current study, water-uptake reductions reached 34.4% in Scots pine and 29.7% in beech.

Assessment of the resistance of mineralized wood against decay fungi

For each test product, the median mass loss after 16 weeks of exposure to the fungal strains was calculated for each set of specimens. The mass loss and final moisture content of the specimens are presented in Table 3.

Table 3 Results of testing the resistance of mineralized Scots pine against basidiomycete fungi

Product	series°	Mean final moisture content [%]		Median corrected mass loss after 16 weeks [%m/m]	
		CP	PP	CP	PP
HM1	treated	24.95	31.88	-1.44	3.37
	untreated	35.80	38.60	21.52	20.86
HM2	treated	66.65	48.13	-0.54	0.60
	untreated	45.20	56.40	54.86	48.23
Virulence controls		39.60	40.66	37.98	25.99

The mean mass loss recorded for the virulence control specimens was >20%, the test was thus considered to be valid.

The negative mass loss values presented in Table 3 were due to the variability of the individual weight gains of the mineralized specimens used for determining the correction factor to be applied to blocks exposed to fungi (±0.7g per treated specimen with HM1 and ±0.2g with HM2). We consider that negative values are not significantly different from zero.

The mean mass losses estimated for samples impregnated with HM1 and HM2 and exposed to both fungal strains were very low. The maximum was reached for HM1 and HM2 treated samples when exposed to *Poria placenta* (3.37 % and 0.60 %).

Following the criteria of the EN 350-1 standard, the rating of the wood's natural durability to basidiomycete fungi (durability class DC from "1 – Resistant" to "5 – Not resistant") is based on the median ML determined for the test specimens exposed to the fungus causing the greatest damage. The median ML calculated with the samples treated with HM1 and HM2 allowed them to be classified as durability class 1.

The final moisture content determination of the samples exposed to fungi showed interesting results. Samples treated with HM1 and exposed to CP showed a mean moisture content of 24.95% (while 35.80% was measured in the untreated controls), which is a bit low to allow fungal degradation. This observation is consistent with the results of the long-term water uptake of HM1 mineralized samples, suggesting a hydrophobic effect of this product, preventing fungal degradation. Samples treated by HM1 and exposed to PP reached a moisture content at the end of fungal testing which was a bit higher than for CP (31.88%), but still lower than for untreated specimens (38.60%).

Conversely, both MH2 mineralized specimens and untreated specimens kept in the same jar showed high moisture contents. Untreated specimens exposed both to CP and PP reached a higher moisture content than the ones of the HM1 mineralized wood blocks (45.20% with CP and 56.40% with PP). However, despite their high moisture content (66.65% with CP and 48.13% with PP), the HM2 mineralized specimens were found to be resistant to decay, suggesting that the product itself has a fungicidal effect.

Assessment of the resistance of mineralized wood against subterranean termites

The resulting attacks on the test specimens impregnated with HM1 and HM2 were observed and compared with those of control test specimens. Termite survival rate and the results of the visual ratings are presented in Table 4.

Table 4: Results of testing the resistance of mineralized wood against termite degradation

Test specimens	Wood species	Mean termite survival %	Ratings
HM1	Scots pine	0%	0 (all specimens)
HM2	Scots pine	52.9%	4 (all specimens)
	Beech	0%	2 – 1 – 2
Untreated control	Scots pine	82.9%	4 (all specimens)

All control specimens were rated “4” after visual examination and the survival rate of the corresponding control colonies was above 50%, validating the test.

Both products demonstrated an effect on termite survival and on the typology of damage recorded (Figure 2). HM1 appeared to protect wood from subterranean termite degradation in the conditions of the test, all test specimens being rated 0 (no attack) after 8 weeks exposure. Furthermore, 100% mortality was recorded at the end of the test, the mortality curve shape (not shown) indicating that termites progressively starved to death as no other source of wood was provided during the test. HM2 impregnated on Scots pine samples did not prevent termite damage (all specimens were rated 4). However, termite survival was lower than for the untreated control (52.9%), indicating a possible effect of the test product. Furthermore, an aspect of the degradation recorded was very unusual, with termites forming cavities in the wood samples without extensively damaging the surface.

HM2 impregnated on beech samples did not fully prevent termite attack but significantly lowered the level of degradation compared to untreated samples (2 ratings 2 and 1 rating 1). This could indicate that the mineralizer improves resistance against termites but that their quantities and/or distribution into wood specimens were not sufficient or not homogeneous enough to fully protect the wood blocks. 100% mortality was recorded after 8 weeks of exposure, indicating either a starvation effect or an impact of the test product on termite survival.

Figure 2: Scots pine samples treated with two solutions with high silica content after being exposed to termites (on the left: HM1; in the middle: HM2; on the right: untreated specimens)

CONCLUSIONS

1. Significant reduction of water uptake capability was obtained with Scots pine and beech specimens impregnated with HM1 and HM2. Both products reduced the water uptake of mineralized Scots pine, HM1 being the most efficient. Conversely, only HM2 reduced the water uptake of beech, while beech mineralized with HM1 showed similar behaviour to untreated wood.
2. Mineralization with both HM1 and HM2 prevented fungal degradation, mineralized Scots pine specimens were found to be resistant to both *Coniophora puteana* and *Poria placenta*. Measurement of the sample moisture content at the end of the test showed that HM1 may have a protective effect by conferring hydrophobic characteristics to the mineralized wood. Conversely, HM2 did not reduce the wood moisture content, suggesting a possible fungicidal effect.
3. Significant improvements in terms of resistance to subterranean termites were obtained with HM1, with the termites being unable to attack, even superficially, the mineralized test specimens. The kinetics of termite mortality indicated that the termites died by starving to death during the test and not as a result of the biocidal effect of the test product. Interestingly, HM2 had no effect on Scots pine but improved the resistance of beech, suggesting different levels of silicate penetration and distribution inside the wood specimens.
4. HM1 mineralizer, initially developed to mineralize materials such as stone and concrete with the aim of decreasing the possible penetration of water into these materials, was demonstrated to be a good candidate product for the development of non-biocidal solutions for the protection of wood against biological threat.

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Comparison of the Surface Checking of Acetylated Pine and the Tropical Hardwood Ipe Exposed to Accelerated Weathering

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Keywords: accelerated weathering, Accoya®, acetylation, decking, Ipe, pine, surface checking

ABSTRACT

The aim of this research was to determine whether acetylated solid pine wood decking (Accoya®), is as resistant to surface checking as decking made from the tropical hardwood Ipe. Replicate acetylated radiata pine, Scots pine and untreated Ipe decking samples were exposed to accelerated weathering over 5 days in a weatherometer designed to accelerate the surface checking of wood. At the end of each 5-day exposure period, samples were conditioned and the length and width of the ten largest checks at the exposed surface of the samples were measured. Checks in acetylated pine samples were small and difficult to see and showed smaller variation in size than those in Ipe samples. There was no statistically significant difference in the sizes of checks that developed in acetylated radiata pine and untreated Ipe samples exposed to accelerated weathering. The checks that developed in the acetylated Scots pine samples were significantly thinner than those in Ipe, although their lengths were not significantly different. We conclude that acetylation reduces the checking of flat-sawn radiata and Scots pine decking boards exposed to artificial accelerated weathering to a level that matches that of the tropical hardwood Ipe, a species that is favoured by consumers for use as exterior decking. Our findings support the use of acetylated radiata and Scots pine as an alternative to tropical hardwoods for residential decking.

INTRODUCTION

Acetylated wood is dimensionally stable and resistant to both fungal and insect attack (Tarkow *et al*. 1946, Peterson and Thomas 1978, Hague *et al*. 2014). There is also strong evidence in the scientific literature that acetylation reduces the surface checking of acetylated *veneer* exposed to natural or accelerated weathering (Tarkow *et al*. 1946, Dunningham *et al.* 1992, Plackett *et al*. 1992). Since these studies were carried out acetylation processes have been commercialised in the Netherlands and USA, by Accsys Technologies and the Eastman Chemical Company, respectively (Hill 2011, Rowell 2014).

The ability of acetylation to reduce surface checking of *solid wood* is important for wood used as outdoor residential decking where consumers prefer decking products that do not develop large surface checks that mar the appearance of the decking (McQueen and Stevens 1998). Decking made from tropical hardwoods such as teak (*Tectona grandis* L.f)) and Ipe (*Handroanthus* spp.) is highly regarded by consumers, in part, because it checks less than other species when exposed to the weather (Williams *et al.* 2001). However, the supply of some tropical hardwoods is not sustainable and, as a result, there is strong interest in developing modified products from wood derived from sustainably managed forests that can match the performance of tropical hardwoods.

With this desirable outcome in mind, we sought to determine whether acetylated solid pine wood decking (Accoya®), which is now readily available around the world, is as resistant to surface checking as the tropical hardwood Ipe, a species that is much sought after by consumers for use as exterior decking.

EXPERIMENTAL

Four acetylated flat-sawn radiata pine (*Pinus radiata* D.Don) samples and similar numbers of acetylated flat-sawn Scots pine (*Pinus sylvestris* L.) and untreated Ipe samples were provided by Accsys Technologies. The acetylated 'Accoya®' samples were chemically modified to a weight gain of approximately 20% by Accsys Technologies at their factory in Arnhem, the Netherlands. All samples measured 400 mm (longitudinal) x 100 mm (tangential) x 22 mm (radial). A 4.8 mm diameter hole was drilled into all four corners of each sample. The diameter at the top of each hole was enlarged to 9.6 mm with a countersink drill bit. Each hole was positioned 40 mm from the end grain and 25 mm from the sides of the sample.

Samples were conditioned for 5 days at 20 ± 1°C and 65 ± 5% r.h. in a constant climate control room. Two samples were selected at random and secured bark-side up to a wooden frame in a rectangular Perspex holder using coated, corrosion resistant, deck screws (8 x 2" H. Paulin High Performance Duradized II). The samples were exposed to accelerated weathering over a period of 5 days in a weatherometer, specifically designed to accelerate the surface checking of wood. This process was repeated until all 12 samples were weathered. The weathering cycle involved exposure to repeated wetting and drying and UV light for 5 days as described by Ratu and Evans (2008). At the end of each 5-day exposure period, the samples were conditioned at 20 ± 1°C and 65 ± 5% r.h. for 5 days, and the length and width of the ten largest checks at the exposed surface of the samples were measured using a transparent Perspex ruler and an optical magnifying glass containing a calibrated graticule, respectively.

Check length, width and area was subjected to an analysis of variance to examine whether differences in check sizes were significantly different between the three species. Statistical computation was performed using Genstat v. 12.1 (VSN International 2009). Results are presented in graphs, and each graph contains error bars representing 95 percent confidence intervals that can be used to assess whether differences in check sizes between species are statistically significant.

RESULTS AND DISCUSSION

The average length, width and area of the ten largest checks in weathered specimens are plotted in Figures 1, 2 and 3, respectively. The average length of checks in Ipe and acetylated radiata and Scots pine samples were 29.6, 28.3, and 34.0 mm, respectively (Figure 1). These differences were not statistically significant (p=0.482). The weathered samples mostly developed narrow checks and the average width of checks in Ipe and acetylated radiata and Scots pine samples were 0.087, 0.076, and 0.026 mm, respectively. Checks in acetylated Scots pine samples were significantly narrower than those in the other two species (Figure 2).

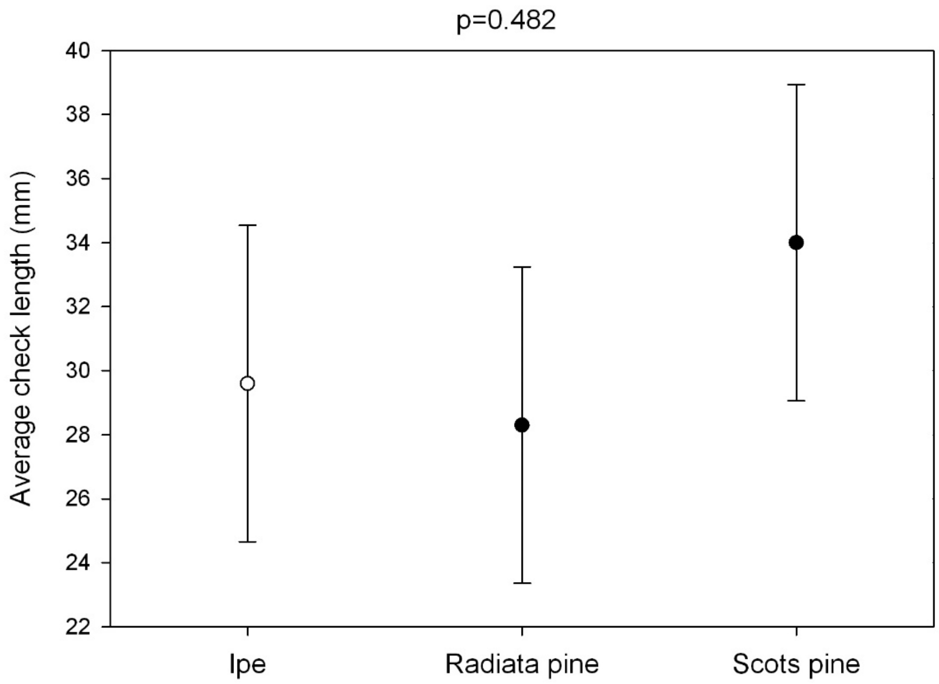

Figure 1: Average length of checks in acetylated pine samples and untreated Ipe samples after 5 days of accelerated weathering

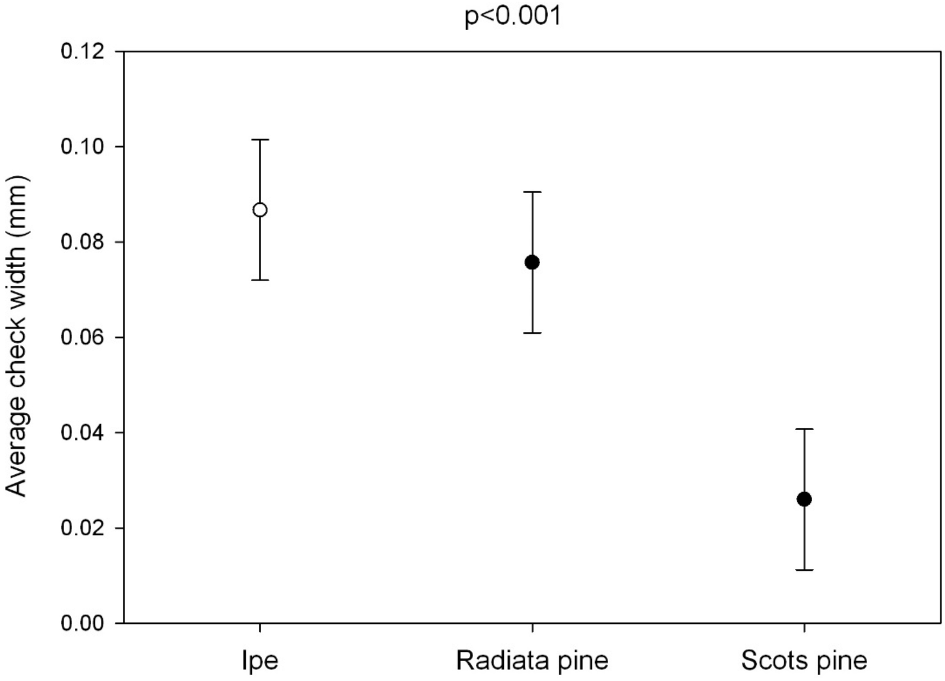

Figure 2: Average width of checks in acetylated pine samples and untreated Ipe samples after 5 days of accelerated weathering

The average area of checks in Ipe and acetylated radiata and Scots pine samples were 4.39, 2.17, and 0.93 mm^2, respectively. The average area of checks in acetylated Scots pine samples was significantly ($p<0.05$) smaller than those of checks in Ipe (Figure 3). The average area of checks in acetylated radiata pine samples was also smaller than that of checks in Ipe, but the difference was not statistically significantly ($p>0.05$) (Figure

3). Most of the checks that developed in the acetylated samples during weathering could not be seen from a height of 1.5 metres, and therefore they would not affect the appearance of wood used as decking.

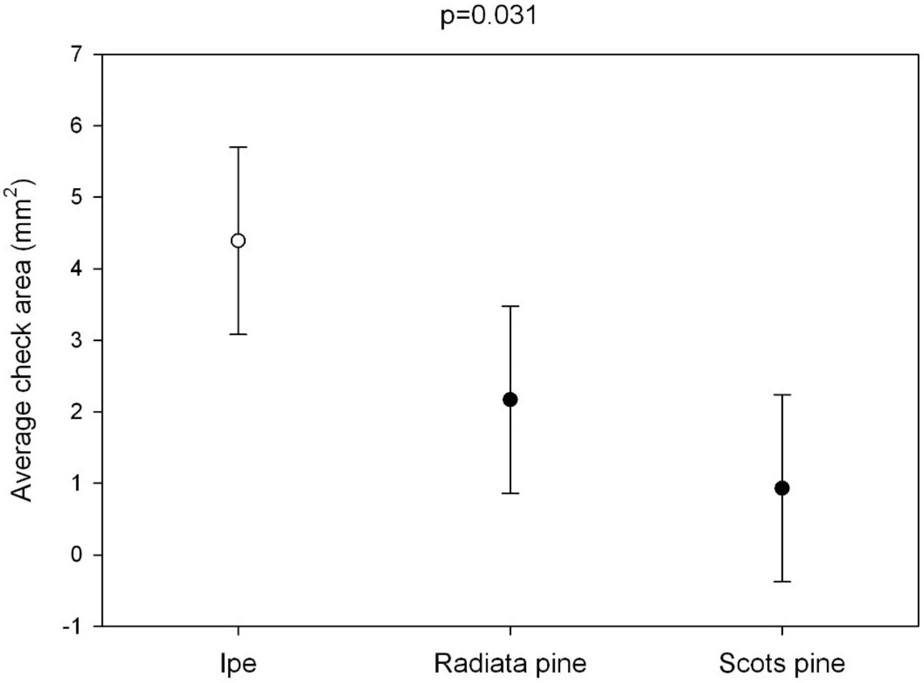

Figure 3: Average area of checks in acetylated pine samples and untreated Ipe samples after 5 days of accelerated weathering

One of the Ipe samples developed large checks, but even these checks were difficult to see because of the lack of contrast between the checks and the natural dark brown colour of Ipe. One of the Ipe samples also exuded gum-like extractives during accelerated weathering which left spotty black, crud-like deposits on the surface of the weathered specimen. All of the acetylated pine samples became slightly darker and yellower, as expected, after they were weathered.

The area of the checks that developed in the weathered Ipe and pine samples can also be seen in Figure 4. This figure is a box-plot showing the distribution of check sizes for the different samples. The top and bottom of each grey box represent the 75th and 25th percentile, respectively. The top and bottom of each fenced bar represent the 90th and 10th percentile, respectively. The median and means are the solid and dotted lines that generally lie within each box. The open circles on the graph are outliers that lie outside the fenced bar. Two of these outliers are the visible checks that developed in Ipe (mentioned above and arrowed in Figure 4).

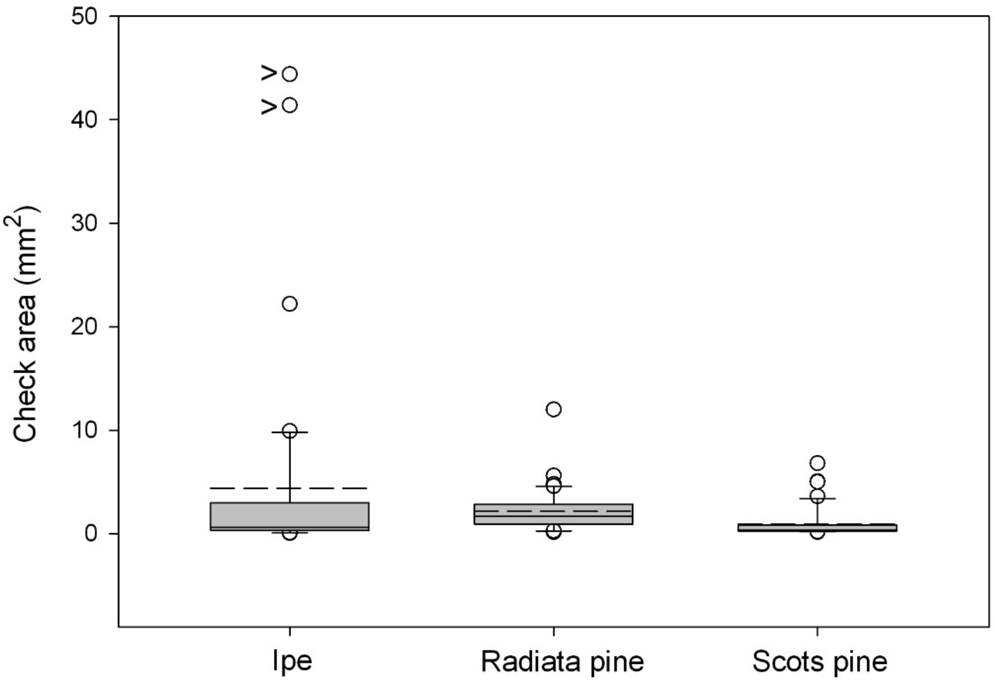

Figure 4: Box plot of area of checks in acetylated pine samples and untreated Ipe samples after 5 days of accelerated weathering. The arrows indicate that individual checks represented by open circles affected the appearance of boards

The box plot of check area shows that acetylated Scots pine samples had the smallest variation in check areas, which is a desirable property for a material destined for markets where end-users will expect the acetylated wood to perform consistently (Figure 4). In contrast Ipe showed larger variation in check area, due to the development of large checks in one of the samples that was tested, as mentioned above.

CONCLUSION

We conclude that acetylation reduces the checking of flat sawn radiata and Scots pine decking boards exposed to artificial accelerated weathering to a level that matches that of the tropical hardwood Ipe, a species that is sought after by consumers for use as exterior decking. Our findings support the use of acetylated radiata and Scots pine as an alternative to tropical hardwoods for residential decking.

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Laboratory and Marine Trials of Resistance of Furfurylated Wood to Marine Borers

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Keywords: furfurylation, chemical modification, wood borers, *Limnoria*, shipworm

ABSTRACT

New approaches are needed to prevent borer attack in wood intended for use in the marine environment, because traditional treatments are restricted or prohibited in this end use. Wood modification is a promising alternative, but the modification processes may require optimisation for marine end use. The standard testing method as defined by EN 275 requires long term marine testing in which an iterative approach to process refinement is not feasible. This study used rapid laboratory testing protocols and marine tests to evaluate the efficacy of furfurylation in reducing attack by marine wood borers. Laboratory trials provided rapid assessment of potential treatments under controlled conditions, whilst marine trials provide more robust long term results under realistic exposure conditions. The wood samples were treated with one of three proprietary procedures for inducing polymerisation. Established methods for testing with the boring crustacean *Limnoria* allowed comparisons to be made with known timber species with a reputation for durability under marine conditions. Wood modification was shown to achieve useful reductions in the feeding rate and survival of test organisms. Statistically robust results were obtained within four weeks. New methods for assessing the effects of wood modification on settlement and subsequent growth by shipworms yielded similarly robust and rapid results. The findings were compared with data for the same wood modifications obtained in a standard marine trial. Field and laboratory findings were in broad agreement. The laboratory methods were shown to be suitable for iterative optimisation of modification.

INTRODUCTION

Wooden structures in seawater can become rapidly degraded by attack from marine borers which use the wood as their food source and habitat. In Europe, the marine wood boring species that pose the most significant threat are from the bivalve mollusc family Teredinidae (shipworms) and the isopod crustacean family Limnoriidae (gribble) (Borges *et al*. 2014 a, b). Both types first break wood down mechanically: shipworms with their ridged shells and gribble with their cutting and grinding mouthparts. The wood is then digested via a suite of enzymes, glycoside hydrolases and others, which enable the borers to depolymerise polysaccharides (King *et al*. 2010; O'Connor *et al.* 2014).

Preservation of wood using broad spectrum biocides such as creosote or chromated copper arsenate (CCA) has, until recently, provided economically-viable protection against borer attack. However, legislation, such as the EU directive affecting CCA treatment (European Commission 2003), limits the use of these broad spectrum biocides in the marine environment. Tropical hardwood species that display natural durability to borer attack often come from unsustainable sources and logging is consequently restricted. The development of a non-toxic yet effective method of wood preservation is thus urgently needed. The chemical modification of wood as a means to inhibit biodegradation offers a promising solution since modification only affects organisms ingesting the wood. The effective use of furfurylation is well established (Amaury *et al.* 1988, Anaya *et al.* 1984, Goldstein and Dreher 1960, Westin 1996). In this process, molecules of furfuryl alcohol become polymerised within the cell walls resulting in the improvement of desirable properties of wood such as dimensional stability and hardness (Lande *et al.* 2004), which may also aid resistance to biodegradation. More recently, the modification method has been adapted (Westin 1996) and in tests, the resulting leachate produced demonstrate lower toxicity units (TU) when compared to restricted broad spectrum biocides such as CCA (Pilgard *et al.* 2010). In addition, modification of wood with furfuryl alcohol is an economically and environmentally attractive method since furfuryl alcohol can be derived from renewable biomass such as corncobs or sugar cane (Lande *et al.* 2008).

This project set out to assess the effectiveness of three furfuryl alcohol treatment processes as methods for increasing resistance to marine wood borers. The animals selected for laboratory assessment were those found to pose a widespread risk in European waters: the shipworm *Lyrodus pedicellatus* and the isopod *Limnoria quadripunctata* (Borges *et al*. 2014 a, b). Laboratory trials were used to measure durability in terms of reduction of feeding and increase of mortality rates of *L. quadripunctata* (Borges *et al*. 2009), and reduction of settlement capabilities of *L. pedicellatus larvae*.

EXPERIMENTAL

Timber from maple (*Acer platanoides)* and pine (*Pinus radiata)* was cut into planks. Part of each plank was treated and part untreated to provide within-plank control for each treated sample. The planks from each species were impregnated, cured and dried with schedules designed to control polymerisation within the wood. Three treatment and polymerisation processes, designated in this paper as A, B and C were tested.

Laboratory feeding trial with **Limnoria quadripunctata**

Test sticks measuring 20 x 5 x 2 mm were produced to provide five replicates per plank; twenty five replicates of each treatment process/wood species combination, giving a total of three hundred test sticks. The test sticks were placed in separate beakers (5 replicates per beaker) containing 500 ml unfiltered seawater collected from Langstone Harbour and leached for three weeks with a water change after two weeks. The sticks were then placed, one per well, into 12 well cell culture dishes. The arrangement of the treatments and wood species within the dish was determined using a pseudo Latin square design to ensure that each sample was represented in each well position at least once. Five ml of seawater was pipetted into each of the cell wells and the cell culture dishes were placed into a light- and temperature-controlled growth room (20±2^{o}C) for four days prior to the start of the experiment.

The specimens of *L.quadripunctata* used in the trials were cultured and maintained in balau (*Shorea* sp.) wood samples collected from the intertidal zone at Southsea, Portsmouth (Grid reference: SZ 638 984 GB). The wood and the animals were kept immersed in running seawater at Portsmouth Institute of Marine Sciences for approximately three months prior to the start of the experiment.

Three hundred animals were extracted from balau wood and incubated in a growth room at 20±2 ^{o}C in seawater collected from Langstone Harbour for three days prior to the onset of the experiment. The animals were then examined for the presence of rapidly beating pleopods (a sign of vitality), four puncta on the pleotelson (a characteristic of the species) and to ensure that none of the animals were gravid females. The selected animals were then placed, one per cell, into the cell culture dishes which were kept in the growth room for a total of six weeks. The seawater was changed twice a week at which point the animals vitality and position on the wood was assessed.

Laboratory settlement trial with **Lyrodus pedicellatus** *larvae*

Six boards of wood from each treatment/wood species combination were leached in unfiltered sea water from Langstone Harbour. The boards were placed in an upright radial orientation at the bottom of cylindrical tank of seawater. A board of wood infested with *Lyrodus pedicellatus* actively releasing larvae was positioned within the tank for a period of 24 hours. Hemispherical pits created by larvae attempting to settle were counted under stereo microscope. Numbers of animals that had bored into and settled within the wood were recorded using X-rays.

Marine trial

Test boards measuring 25 x 75 x 200 mm were attached to frames in a ladder-like structure (Figure 1) and submerged at Olhão harbour, Portugal. After a period of six months the boards were removed from the harbour, fouling was detached and limnoriid attack visually assessed and rated according to EN 275 (1992). The boards were X-rayed in order to assess attack by teredinids using EN275 ratings (Figure 2). Boards that were deemed a ‘fail’ (rating 4) were replaced.

Figure 1: Boards of treated and untreated wood after submersion in Olhão harbour, Portugal for six months

Figure 2: X-rays of boards of treated and untreated wood after submersion in Olhão Harbour, Portugal for six months. Shipworm attack is visible in panel 308(pine control)

RESULTS AND DISCUSSION

Laboratory feeding trial with **Limnoria quadripunctata**

Both treatment and wood type significantly affected faecal pellet production (Figure 3), but no effects specific to individual planks were detected. Animals fed on untreated maple and pine wood produced more pellets per day than those fed on modified wood, with pellet production significantly higher on pine than maple (GLM ANOVA with wood species and treatment as factors, Tukey's post hoc test). Animals fed on wood with treatment C produced significantly less pellets than those fed on wood with the other treatments. The feeding rates are comparable to those observed in previous trials that tested chemically-modified wood as a means to increase resistance to attack by limnoriids (Borges *et al.* 2008) and in some, demonstrate a higher resistance (Papadopolous *et al.* 2008).

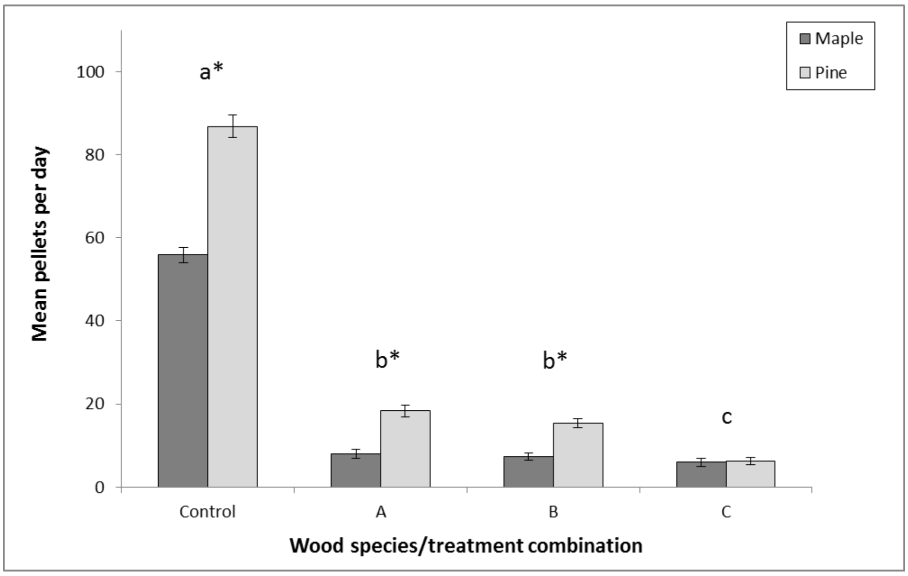

Figure 3: Effect of wood species and treatment on faecal pellet production by **L. quadripunctata** *over a period of six week. (p<0.0005; Tukeys post hoc pair wise test of a GLM ANOVA model using treatment and wood species as fixed factors). Treatments that do not share a letter are significantly different. Asterisk indicates significant difference between wood types for a particular treatment.*

Less than 10% of the animals fed on the control boards of either wood species died during this experiment, but the mortality of animals fed on treated maple boards was more than 80%, whilst the mortality of animals fed on treated pine boards with treatments A or B was 40-50% and with treatment C was over 80% (Fig. 4). Mortality on the treated wood was markedly higher than reported for animals fed on other wood with other modifications in previous trials (Papadopoulos *et al.* 2008, Klüppel *et al.* 2010) with comparable results to a trial with wood modified with DMDHEU and phosphobutane tricarboxylic acid (Borges *et al.* 2004).

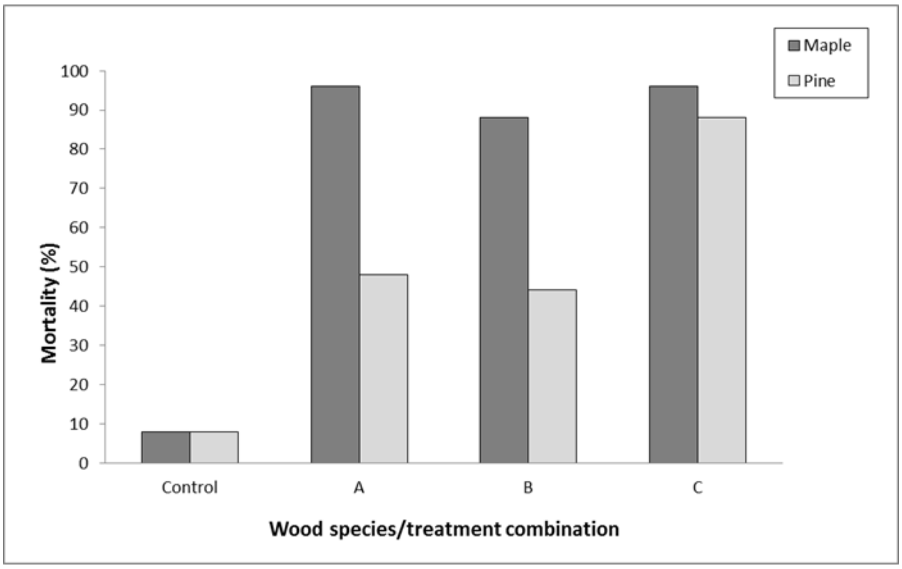

Figure 4: Effect of wood species and treatment on mortality of **Limnoria quadripunctata**

Laboratory settlement and growth trial

The highest numbers of larval settlement attempts were observed on untreated pine wood whilst the least amount of attempts was observed on experimentally treated maple (Fig. 5). Overall, as with the feeding trials, the treated maple wood was more resistant to settlement than the treated pine wood. However, the experiment will need to be optimised and repeated as unexpectedly low numbers of live animals (<5) had successfully invaded the control wood samples and many dead juveniles were observed.

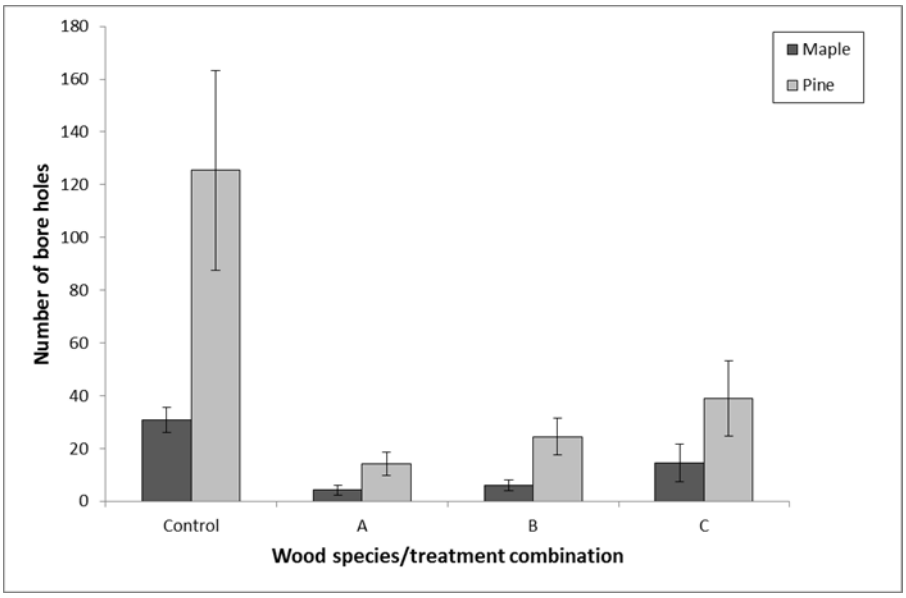

Figure 5: Effect of wood type and treatment on intensity of* Lyrodus pedicellatus *larval settlement

Marine trial

Untreated boards of maple and pine submerged at Olhão harbour Portugal failed after six months due to attack from both limnoriids and shipworm. However, both the naturally durable test wood azobé, and the boards of maple and pine treated with one of the three proprietary formulas either reduced or prevented attack (see Fig. 6).

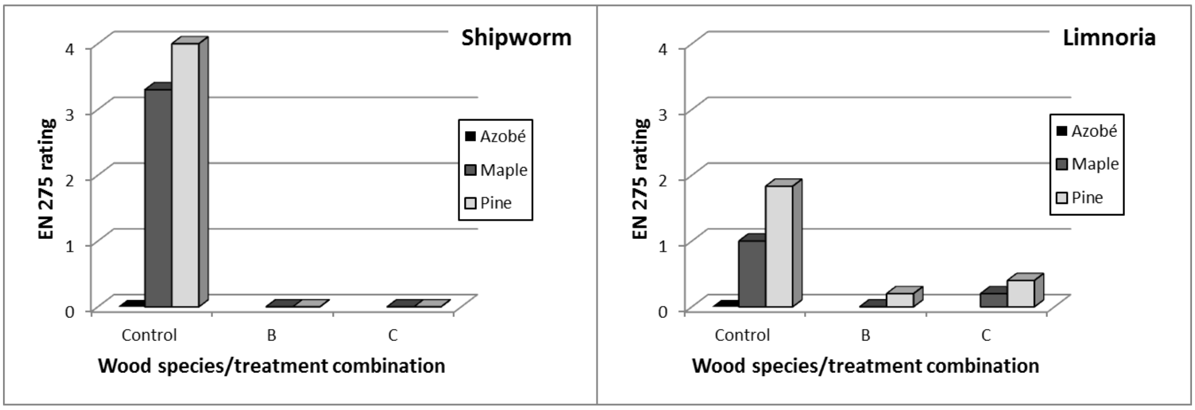

Figure 6: EN275 attack ratings of wood submerged at Olhão harbour after six months

CONCLUSIONS

Furfurylation of maple and pine wood markedly reduced attack both by crustacean and by bivalve borers. In laboratory trials the treatments inhibited the ability of shipworm larvae to settle on and tunnel into the wood. The laboratory observations match initial findings in the marine trial. The settlement test with *L. pedicellatus,* however, requires optimisation to improve the numbers of animals involved in the test and the condition of the wood tested. The marine trial needs to be continued to a duration of five years in order to satisfy the test standards set out in EN275, but laboratory trials will permit optimisation of treatment methods over a much shorter period.

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