

**PROCEEDINGS OF  
THE FIRST EUROPEAN CONFERENCE  
ON WOOD MODIFICATION**



The European Thematic Network for Wood Modification  
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Ghent, Belgium 3rd - 4th April 2003



*EDITORS: Joris VAN ACKER and Callum HILL*



EUROPEAN COMMISSION  
DIRECTORATE GENERAL RESEARCH



# **THE FIRST EUROPEAN CONFERENCE ON WOOD MODIFICATION**

## ***ECWM 2003***

Edited by

**Joris VAN ACKER and Callum HILL**

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## The First European Conference on Wood Modification (April 3-4, 2003)

Thematic Network for Wood Modification  
(contract N°: G1RT-CT-2000-05002)

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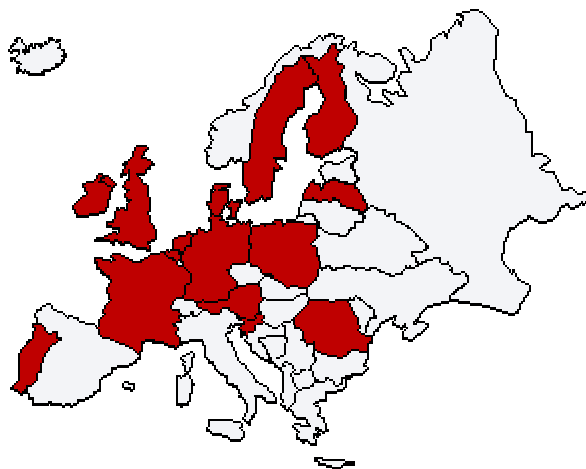
## Preface

Dennis Jones

The wood processing sector faces many challenges. Increasing quantities of plantation grown softwoods are being processed, which generally have inferior properties compared with timber sourced from virgin forests. There is intense competition from non-sustainably derived materials (such as uPVC) which are entering markets that have traditionally been dominated by timber products. Environmental concerns are leading to the phasing out of traditional wood preservatives, which rely upon toxicity as their primary mode of action. In order to maintain the competitiveness of wood, new approaches are needed. Research into wood modification is one way of meeting these challenges.

Wood modification involves a treatment of wood to enhance its properties, but does not involve the production of a product that contains toxic residues. Thus a modified wood product can, at the end of its life, be disposed of or recycled, without a negative impact upon the environment. Various approaches have been investigated, some of which have been commercialised, some are near to commercialisation, and some are still at the research stage. This spectrum of activity has been the subject of the Thematic Network on Wood Modification, which is organising this conference.

In order to provide a focus on a European front, the European Commission, through its Fifth Framework programme, funded a project entitled “Wood modification, the novel base, providing materials with superior qualities without toxic residue”, or more commonly known as the Thematic Network for Wood Modification. The duration of the project was from May 2000 to April 2003. The Network consisted of 28 partners from 15 countries. The countries represented are shown in red. The countries represented were Austria, Belgium, Denmark, Finland, France, Germany, Ireland, Latvia, Netherlands, Poland, Portugal, Romania, Slovenia, Sweden and the United Kingdom. These partners represented different elements of the timber sector and cover private companies, research institutions and universities. Due to the diverse interests of these partners, there was no ‘fixed’ goal, only the improvement in the technologies, facilities, evaluations and eventually the choice of the end-user.



*Countries taking part in the Thematic Network for wood modification*

Wood modification may be achieved through three differing methods; chemical, thermal or enzymatic modification. Some of the partners within the Network have experience or businesses directed towards these techniques. The aim of this network was to increase awareness of work going on at the European level and to increase collaboration. This will accelerate development and subsequent commercialisation.

The Network was split into 6 distinct sections (known as work packages). These represent the areas where a concerted effort was placed in deriving future policies and methods to benefit the European Union. Each work package was managed by a single partner (in conjunction with a deputy), these reporting to the overall Network Co-ordinator (SHR Timber Research, The Netherlands). The six work packages were as follows:

1. Management
2. Market
3. Dissemination
4. Chemical Analysis and Modification Agents
5. Process Development
6. Properties and Standardisation

This conference represents one of the key actions within work package 3. Attendance of this conference extends beyond the membership of the Network, indicating the current interest in wood modification. During the two days of this conference we will learn of many new processes. Some of these are already approaching commercialisation, others are still at the laboratory demonstration stage. Some of these may be presented as commercial processes in future wood modification conferences. The European Commission has provided a platform encouraging the development and marketing of new methods for treating wood. Through this and subsequent conferences, it is our intention to keep up this momentum, where we will see modified wood products regularly in the market.

Dennis Jones

Network Co-ordinator

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**OIL AND HEAT TREATMENTS**  
ORAL PRESENTATIONS



## Improvement of Wood Properties by a Combined Impregnation Process – the Royal Process

A. Treu<sup>1</sup>, J. Habicht<sup>2</sup>, R. Klaucke<sup>3</sup>, H. Militz<sup>4</sup>

<sup>1</sup> University Göttingen, Institute of Wood Biology and Wood Technology, Germany, atreu@gwdg.de

<sup>2</sup> Dr. Wolman GmbH, Sinzheim, Germany, joerg.habicht@wolman.de

<sup>3</sup> Dr. Wolman GmbH, Sinzheim, Germany, rudolf.klaucke@wolman.de

<sup>4</sup> University Göttingen, Institute of Wood Biology and Wood Technology, Germany, hmilitz@gwdg.de

**Keywords:** dimensional stability, mechanical properties, oil treatment, wood preservative, weathering performance, water repellency

### ABSTRACT

This paper focuses on the improvement of wood properties of pine and spruce using a combined wood preservative - oil treatment, known as the Royal process. The treated products were analysed for their preservative- and oil-retention, as well as for important wood properties like wood moisture content, durability in natural and artificial weathering conditions, surface appearance and mechanical properties. For testing the mechanical performance of treated pine wood samples the bending and the impact bending strength was measured. The treatment showed no evident reduction of strength neither for small nor for large samples. Artificial weathering tests and one year outside exposure tests showed a considerable reduction of water uptake in Royal treated pine and spruce wood samples compared to untreated and samples treated with a conventional wood preservative. A lower effect in reduction of water uptake for spruce wood samples using the combined process could be explained by the reduced uptake of oil for spruce wood samples. The cracking behaviour and the surface appearance was evaluated during the outside exposure of the samples. A reduction in cracking for treated samples was assessed. The discoloration of the surface was reduced to a slight degree but after one year of outside exposure a distinct greying was observable. Finally, the costs of the process are compared to alternative treatments and the market chances for different applications are evaluated.

### INTRODUCTION

The natural durability against wood destroying microorganisms for most of our economically important wood species is limited. An increase in durability is therefore required if such wood products shall be used for above ground, or in ground applications.

The impregnation with modern wood preservatives can enhance resistance against wood destroying fungi. However, the durability of a wood product (*e.g.* for cladding, decking, garden furniture, noise barriers, fences etc.) is influenced by different factors, not only by the effectiveness of biocides or the natural durability of the wood against microorganisms, but furthermore by factors like cracking behaviour of the wood product, the UV-stability, and moisture uptake of the wood.

Oil and water repellents are well known in different applications. As wood treatments they are beginning to attract more interest for practical applications especially in combination with known wood preservatives. Because of their water repellent effect they can improve the

hydrophobicity of surfaces of wood. Therefore they also have a positive effect against leaching of preservative compounds.

Several authors report results from durability tests against micro-organisms on wood samples treated with different natural oils only (Sailer 2001, Olsson *et al.* 2001). Their findings indicate that an oil treatment alone (even at higher retention) does not increase the resistance of non durable wood species like pine and spruce sufficiently for most outside applications. Results from comparative durability tests both in laboratory and field trials on the systems proposed in this paper will be reported later.

The effect of linseed oil on wood having water repellent characteristics is well known (Borgin *et al.* 1970). However, the consistence and the long term stability of the oil is important for practical use.

The combination of a basic impregnation with a wood preservative and the subsequent treatment with a modified natural oil at elevated temperature was developed some 25 years ago (Häger 1980), usually referred to as the “Royal Process”. Only recently there has been increasing interest in this technique both on the scientific and commercial side (Treu *et al.* 2001).

In our study, the performance of a product treated with a combined impregnation process, including an oil impregnation with high temperatures was tested, not only for its water uptake behaviour and weathering performance, but also for its mechanical properties.

The optimisation of the process parameters and their correlation with the improved material properties are also subject of ongoing research work and will be reported later.

## MATERIALS AND METHODS

The products of a combined impregnation process (CIP) were tested for their weathering performance exposed to artificial and natural weathering. Furthermore, the mechanical properties such as bending strength, modulus of elasticity (MOE) and impact bending strength were tested on small bar samples and bigger board samples (only bending strength), according to DIN 52186, DIN 52189 and EN 405. For comparison, wood samples treated with a chromium free wood preservative (CFWP), modified linseed oil (mod. L.) alone, as well as untreated control samples were tested.

The combined impregnation process (CIP) includes two process steps: 1. A simplified impregnation procedure (“Lowry process”) with a copper based chromium free wood preservative (CFWP). The process parameters for this step are: 1 hour pressure phase (12 bar) and 20 min vacuum (100 mbar) at the end of the process. This process was chosen to yield a good penetration through the tissue and a preservative coating on the lumen-side cell wall surface, while leaving the cell lumina empty. The solution uptake is generally significantly lower compared to a usual full cell process. After the chemical treatment, the samples were stored overnight for fixation. In the second step of the CIP the wood samples were treated with hot oil (mod. L.) in a vacuum (80° C, 100 mbar) for approximately 5 hours. This step served the purpose to dry the wood down from nearly wet state to a wood moisture content of 12 – 20 % and to hydrophobicise the surface in order to reduce water uptake and to decrease leaching of wood preservatives.

**Table 1: Retention of modified linseed oil (mod. L.), wood preservative (CFWP) and the combination of both (CIP), mean with standard deviation.**

Test	Treatment	Wood Species	Oil retention [kg/m <sup>3</sup> ]	Retention of CFWP [kg/m <sup>3</sup> ]
Artificial weathering	CIP CFWP	<i>Pinus sylvestris</i>	54 (12,6) -	12,7 (2,5) 12,7 (2,5)
Outside exposure	CIP Mod. L. CFWP	<i>Pinus sylvestris</i>	28 (12,6) 39 (6) -	4,4 (0,5) - 4,8 (0,3)
	CIP Mod. L. CFWP	<i>Picea abies</i>	7 (4,9) 10 (7,7) -	5,2 (2) - 3,9 (0,9)
Bending strength (A)	CIP Mod. L. CFWP	<i>Pinus sylvestris</i>	67 (15,4) 87 (31,5) -	7,5 (0,9) - 7,3 (0,7)
Bending strength (B)	CIP CFWP	<i>Pinus sylvestris</i>	54 (12,6) -	12,7 (2,5) 12,7 (2,5)
Impact bending strength	CIP Mod. L. CFWP	<i>Pinus sylvestris</i>	88 (27,3) 108 (34) -	7,4 (0,6) - 7,2 (0,5)

For impregnation with CFWP only, the first step of the CIP was used. The treatment with mod. L. used the same parameters as the second step of CIP, additionally the samples were impregnated with water (1 hour 12 bar, 20 min vacuum) prior to the oil treatment. The uptake of wood preservative and oil is shown in table 1. The wood preservative used in this study was a water-based chromium and arsenic free preservative system with copper (copper hydroxide carbonate), Cu-HDO (bis-(N-cyclohexyl diazeniumdioxo) copper) and boric acid as active substances. This preservative shows a high degree of fixation within 24 hours after treatment (Dr. Wolman 1998). It should be noted at this point that the results obtained with the CIP are strongly dependent on the preservative type used. Preliminary research has also revealed that other wood preservative systems, especially those containing surface active substances as major part of the formulation, will not yield comparable results. The oil used in our experiments was modified linseed oil commercially available and used in industrial plants using the CIP.

### ***Mechanical properties***

#### **Strength bending test**

The bending strength (A) of small bar samples were tested in a Zwick device and the MOE was calculated. The samples were preconditioned for 10 weeks at 65 % RH and 20° C. The test was carried out with pine wood according to DIN 52186. Furthermore, pine board samples which were treated at Dr. Wolman GmbH, Sinzheim, Germany have been tested (bending strength (B)) within the scope of a Diploma thesis (Larnoy 2001).

#### **Impact bending strength**

The impact bending strength was measured using a pendulum impact testing machine (MFL Prüf- und Meßsysteme). The samples were preconditioned in the same conditions (see strength bending test) according to DIN 52189.

### ***Weathering performance***

#### **Artificial weathering**

For artificial weathering tests, an accelerated weathering tester was used (QUV, Q-Panel Lab Products). The wood samples were weathered for 814 hours (34 days). The full weathering cycle used comprises of three different climate conditions (condensation, light/drying and water spray) in iteration. In the artificial weathering device, the cycle is defined by the following programme:

1. step: 24 hours condensation at 50° C and 100 % RH
2. step: Sub cycle, repeating step 3 and step 4 three times

3. step UV light, 2 hours, 60° C

4. step: Water spray, 1 hour

During an artificial weathering test, pine wood samples (CFWP, CIP, untreated) were weighed after different weathering cycles and their wood moisture content was calculated. The accelerated weathering was interrupted after 171 hours (7 days) for cleaning and servicing and started again with a condensation cycle. The test was continued for another 643 hours.

### **Outside weathering**

For testing the outside weathering performance, differently treated pine and spruce wood samples were vertical exposed on a weathering rack according to EN 927. During the outside exposure, the water uptake of the wood samples was determined in a water submersion test for 30 minutes, 90 minutes, 7.5 hours and 31.5 hours. The samples were preconditioned at 65 % RH, 20° C for one week before testing. The preconditioned samples were evaluated on crack behaviour (classification 0 - 3) and surface appearance such as discoloration and greying.

***Table 2: Classification of cracking used for evaluation of outside exposed wood samples***

<b>Rating</b>	<b>Definition</b>
0	no cracks
1	fine and small cracks, max. 5 cracks < 5 cm
2	more than 5 cracks > 5 cm, less than 5 cracks < 10 cm, no continuous cracks
3	Continuous cracks or more than 5 cracks > 10 cm

***Table 3: Wood samples used in the test programme***

<b>Wood species</b>	<b>Treatment</b>	<b>Dimension [mm<sup>3</sup>]</b>	<b>Replicates per treatment</b>	<b>Test</b>
<i>Pinus sylvestris</i> (50% heartwood)	CIP Mod L. CFWP untreated	18x75x275	5	Artificial Weathering
<i>Pinus sylvestris</i> <i>Picea abies</i>	CIP Mod L. CFWP untreated	15x75x270	10	Outside exposure
<i>Pinus sylvestris</i> (sapwood only)	CIP Mod L. CFWP untreated	20x20x360	10	Bending strength (A)
<i>Pinus sylvestris</i> (sapwood only)	CIP Mod L. CFWP untreated	20x20x300	10	Impact bending strength
<i>Pinus sylvestris</i>	CIP CFWP untreated	25x125x800	67	Bending strength (B)

### ***Materials***

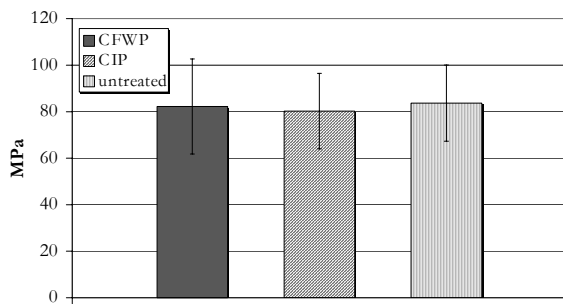
All samples, shown in Table. 3 were planed, except the wood samples for artificial weathering and bending strength (B). They had a moisture content of 12 – 14 % and were free of defects or

any visible signs of fungal attack. The artificial weathering samples were tangential sections whereas the outside weathering samples were radial sections.

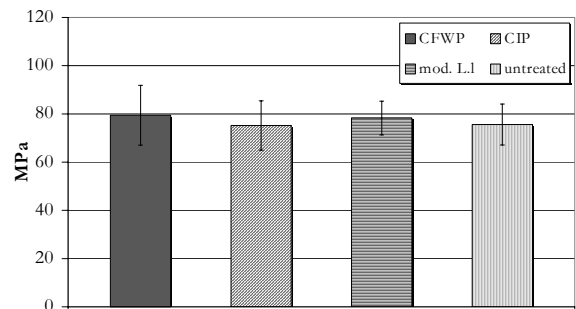
## RESULTS AND DISCUSSION

### *Strength properties*

The strength bending test of small bar wood samples shows values of  $75 \pm 10$  MPa for CIP and untreated samples, approx.  $80 \pm 12$  MPa for CFWP and  $78 \pm 7$  MPa for mod. L. samples. Due to the small number of replicates (10 samples per treatment) a high variation was noticed. In further trials with practical dimensions ( $25 \times 125 \times 800$  mm<sup>3</sup>) and a larger quantity of samples the bending strength was approx.  $80 \pm 16$  MPa for CIP,  $82 \pm 20$  MPa for CFWP and  $83 \pm 16$  MPa for untreated samples. From the bars shown in figure 1 and 2 no difference in bending strength between the differently treated wood samples can be derived. The data are comparable to the literature value of 80 N/mm<sup>2</sup> for pine wood (Niemz 1993).

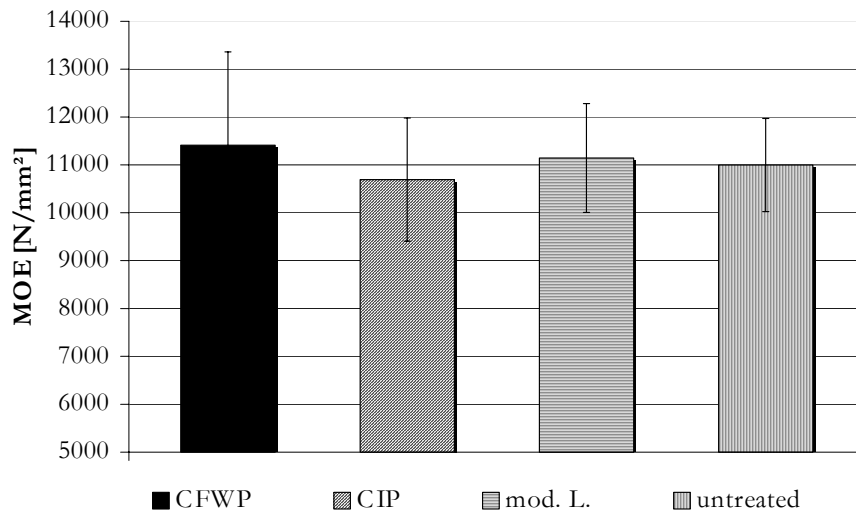


**Fig. 1: Bending strength of pine boards (25x125x800 mm<sup>3</sup>); mean with STD.**



**Fig. 2: Bending strength of pine boards (20x20x360 mm<sup>3</sup>); mean with STD.**

The MOE (see figure 3) determined for untreated pine wood was 11,000 ( $\pm 1,000$ ) N/mm<sup>2</sup> which corresponds to the reference value given in DIN 68364. The MOE's for the treated samples (CFWP, CIP, mod. L.) did not differ significantly from the untreated condition. The impregnation had, therefore, no effect on this strength parameter.



**Fig. 3: Modulus of elasticity (MOE) of pine wood tested; mean with STD.**

Additionally, the impact bending strength was tested. Referring to DIN 68364 pine wood has an impact bending strength of 40 – 70 kJ/m<sup>2</sup>. The untreated samples showed a mean value of  $45 \pm 8$



kJ/m<sup>2</sup> (Fig. 4). Consequently, the treatments had no significant effect on the impact bending strength.

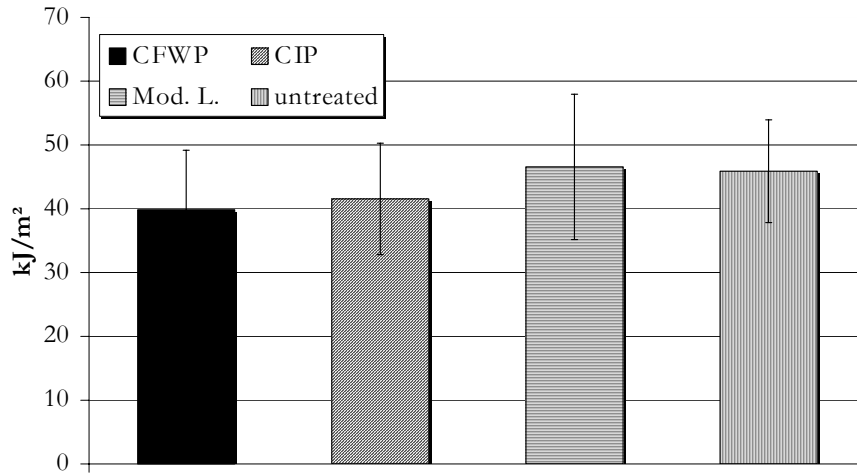


Fig. 4: Impact bending strength of pine wood samples (see fig. 3)

It is known that the treatment of wood with hot oil can influence the mechanical properties of a product. Especially the impact bending strength can be reduced by treatments with temperatures above 180° C. In an oil heat treatment trial at 220° C, Sailer *et al.* (2000) mentioned an impact bending strength loss of pine wood samples of about 50 %. In the process used in our project the temperatures are below 90° C. A negative effect on the mechanical properties can not be stated. Further trials with a larger amount of sample material should be performed to statistically prove these preliminary findings.

**Weathering performance**

The moisture content of CIP samples during the accelerated weathering test was below 30 % whereas CFWP and untreated samples showed a high fluctuation in moisture content from 20 up to 80 % (see figure 5).

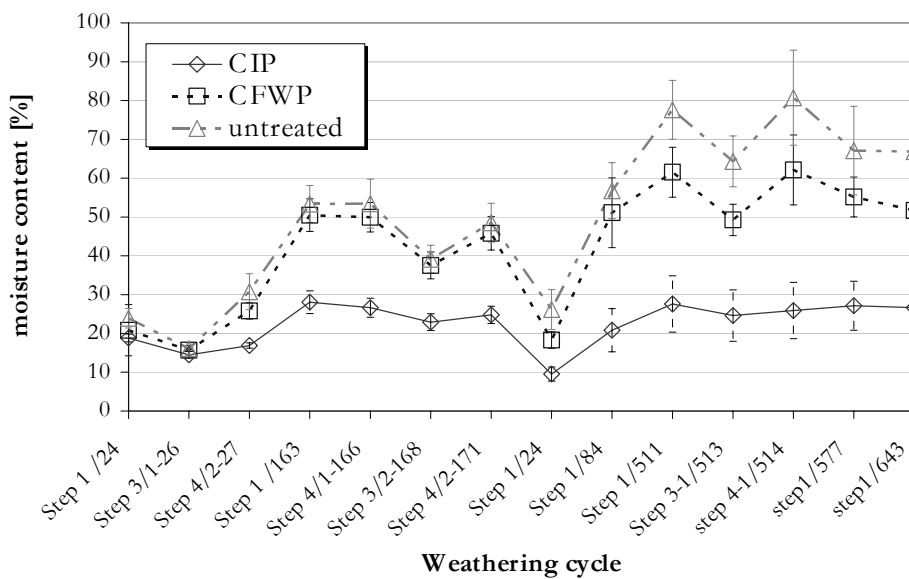
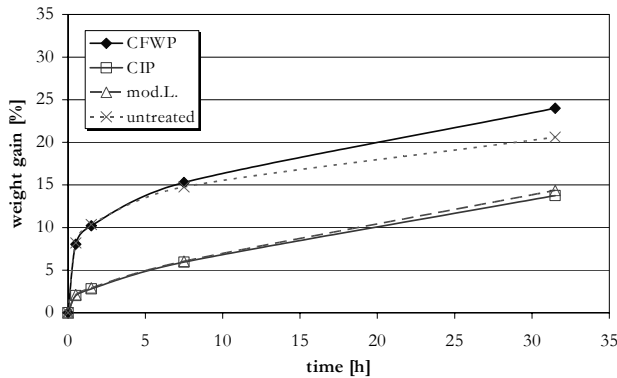


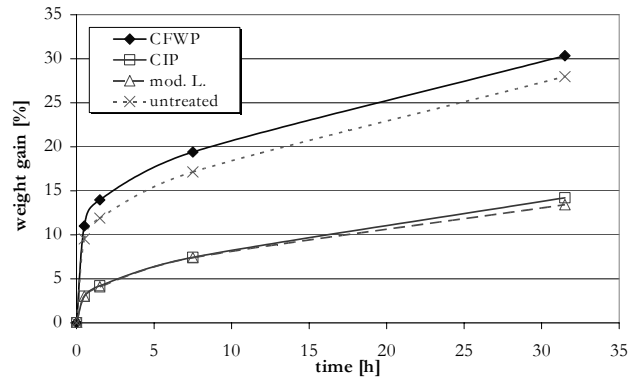
Fig. 5: Moisture contents of wood samples exposed in the accelerated weathering test; mean with STD.

Figure 6 and figure 8 show the water uptake of pine and spruce wood samples at the start of the outside exposure. Untreated and CFWP pine wood samples had 20 to 25 % weight gain after 31.5 hours of submersion, resulting in 30 – 35 % wood moisture content. Oil treated pine samples (CIP and mod. L.) had much less weight gain during the exposure period, resulting in 25 % moisture content.

After 54 weeks of outside exposure, there was still the same water uptake of CIP and mod. L. treated pine wood samples in a submersion test. The water uptake of the CFWP- and untreated samples had increased by approx. 7 %.

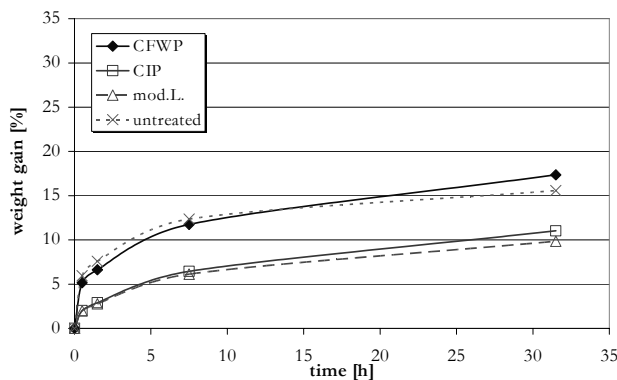


**Fig. 6: Weight gain of pine wood samples during a water submersion test at the beginning of the outside exposure period**

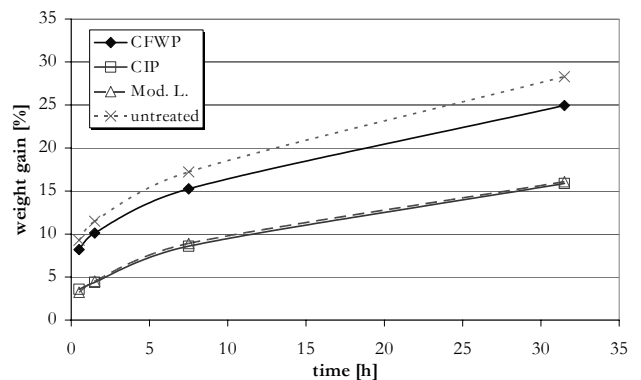


**Fig. 7: Weight gain of pine wood samples during a water submersion test after 54 weeks of outside exposure**

After 31.5 hours of submersion CFWP treated spruce wood and untreated samples had 15 and 17 % weight gain respectively whereas CIP and mod. L. had a weight gain of only 11 and 10 %. The increase of weight gain after 54 weeks of outside exposure is 5% for CIP and mod. L., 8% for CFWP and 13% for untreated samples.

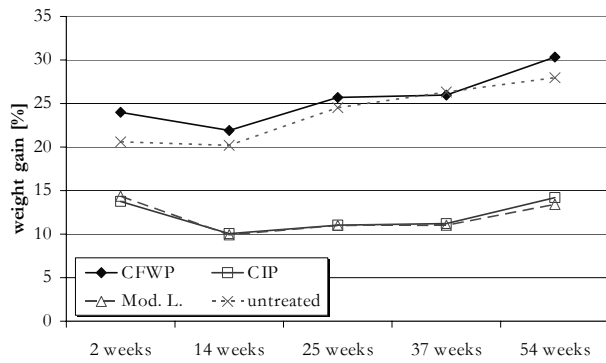


**Fig. 8: Weight gain of spruce samples during a water submersion test at the beginning of the outside exposure period**

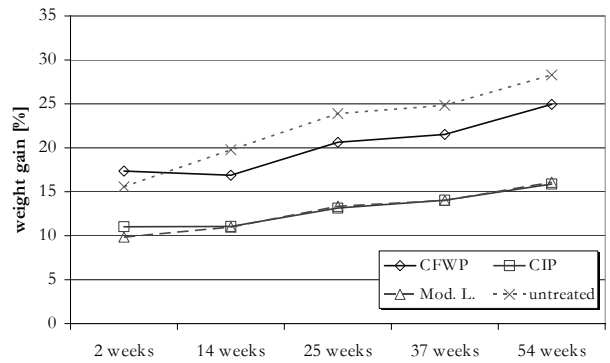


**Fig. 9: Weight gain of spruce wood samples during a water submersion test after 54 weeks of outside exposure**

The lasting water repellent effect of oil treated pine wood (CIP, mod. L.) compared to treated spruce wood was obviously influenced by the oil retention. Oil treated pine samples showed a 4 times higher oil retention than treated spruce samples. Their water uptake after 31.5 hours of submersion is given in figures 10 and 11.



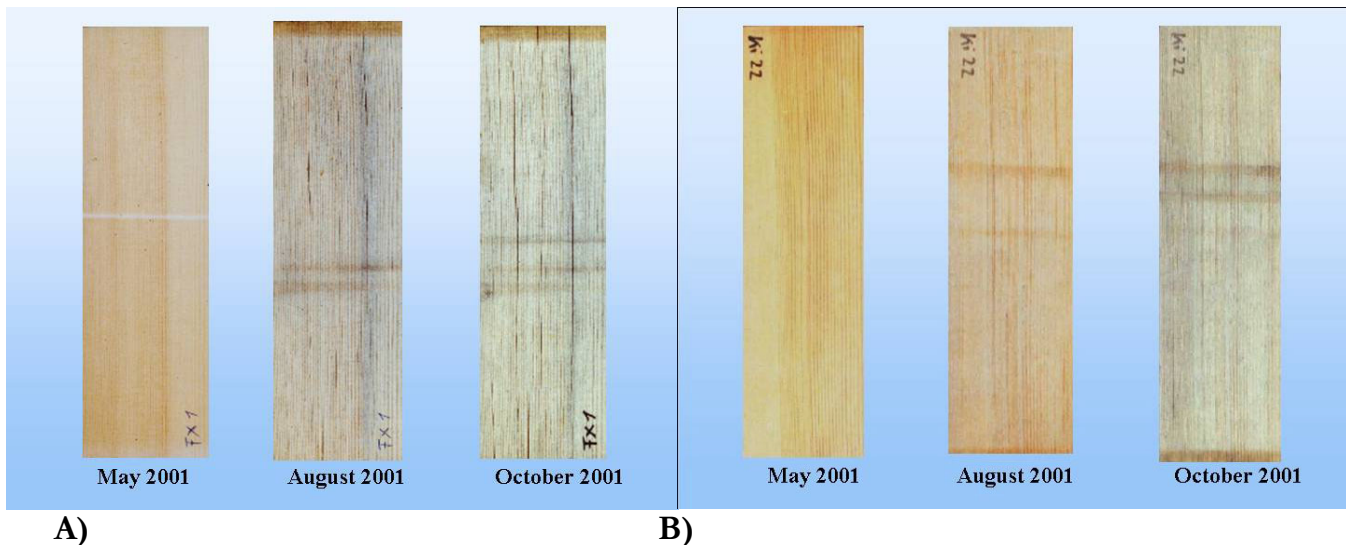
**Fig. 10:** Weight gain of pine wood samples after 31.5 hours submerged in water after 2, 14, 25, 37 and 54 weeks of outside exposure



**Fig. 11:** Weight gain of spruce wood samples after 31.5 hours submerged in water after 2, 14, 25, 37 and 54 weeks of outside exposure

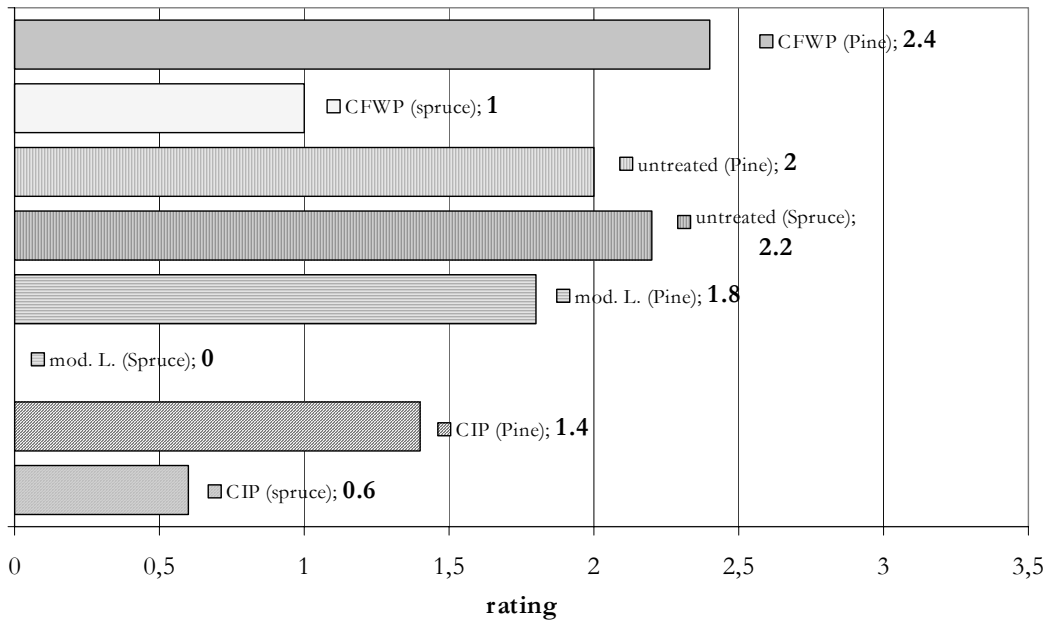
The surface appearance especially the greying of the samples proceeded fast for untreated and CFWP treated samples during the first month of outside exposure. Instead, the CIP and mod. L. impregnated samples showed less discoloration during the first month. Nevertheless a stronger greying of the CIP and mod. L. samples could be observed after one year of outside exposure.

The surface roughness of all CFWP and untreated samples was increased and parts of the earlywood showed signs of physical degradation.



**Fig. 12:** Discoloration of selected untreated [A] and CIP treated [B] pine wood samples after 3 and 5 month of outside exposure

As a result of the evaluation CIP and mod. L. treated pine and spruce wood showed less cracking on the surface than CFWP treated and untreated pine and spruce wood. CIP and mod. L. treated spruce wood samples performed better than treated pine samples so far, although they have a lower oil uptake (see fig 13).



*Fig. 13: Cracking classification of spruce and pine wood samples after one year of outside exposure*

### **Commercial viability**

The CIP requires a conventional vacuum pressure plant for the preservative treatment in the first step. In principle the second step could be performed in the same vessel, but this is usually the more expensive option. Instead, for the oil treatment there are different types in use: Cylinders with square diameters where the wood is lowered into an oil bath, round-shaped ones e.g. as known from former creosote plants or new systems. Based on a small sized commercial plant (annual capacity 2,500 m<sup>3</sup>) typical investment costs for an oil treatment should be scheduled with around 125,000 €. These investment costs are considerably lower than those for alternative techniques.

The production costs (including handling, energy, water but excluding the raw timber and margin) for a typical product (cladding, decking, garden timbers) are in the order of 60-120 €/m<sup>3</sup> compared to 35-50 € for a CFWP treatment alone. For comparison, figures given for a CFWP with a water repellent additive in a one step process are in the order of 55-75 €/m<sup>3</sup> whereas for heat treatment figures of 65-150 €/m<sup>3</sup> are mentioned in the literature (Rapp 2001). With these expenditures low cost commodities are not accessible for wood treated with the CIP. Typical applications where CIP is competitive in price and performance are wooden window frames, cladding, noise barriers, decking, high value garden timbers etc. One big advantage of the system is that no additional surface treatment is required, especially if the oil is pigmented. Other treatments listed except for the combination of CFWP with a water repellent additive usually require a subsequent surface treatment to achieve comparable surface and weathering properties. Due to the penetrating treatment the times between services are longer for the CIP compared to surface treatments.

## **CONCLUSIONS**

The CIP treatment showed no significant change of mechanical properties (MOE, bending strength, impact bending strength) neither for small nor for larger samples. A combined impregnation process which was used on pine wood showed no increase of water uptake in submersion tests after one year of outside exposure. Modified linseed oil treated pine wood

samples had nearly the same water uptake behaviour tested in a submersion test before and after one year of outside exposure, whereas the uptake of CFWP and untreated pine samples was increased. In contrast to pine wood, the water uptake in spruce wood was increased after one year. But there was still a reduction of water uptake of CIP and mod. L. treated spruce samples compared to CFWP and untreated samples (9 – 13 % reduction) after this period.

There is a considerable reduction of water uptake and changing of moisture content on CIP treated pine wood samples compared to CFWP and untreated samples tested in an accelerated weathering tester for 34 days (814 hours). It can be concluded that the water uptake is reduced by the water repellent effect of CIP and mod. L. treatment. The effect of the oil treatment is less pronounced for spruce wood than for pine wood, which could be explained by the reduced uptake of oil but also by the lower initial uptake of spruce wood samples.

In comparison to CFWP and untreated pine and spruce samples, the discoloration of the surfaces of CIP and mod. L. treated samples is slowed down for the first weathering period of half a year. After one year a stronger greying of the treated samples can be observed. Furthermore, the surface roughness of CIP and mod. L. treated samples has not increased in the same manner as CFWP and untreated samples. The classification of cracking shows a reduction in cracking behaviour of CIP and mod. L. treated wood samples after one year of outside exposure.

The production costs of CIP are in the same order of magnitude as alternative treatments offering comparable product properties, while investment costs are relatively low. CIP treated wood should offer a promising alternative for high value out-door applications of timber.

#### ACKNOWLEDGEMENTS

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## Treatment of Wood with Royale Stabilising Oil

Dr. M.R. Powell

Osmose, Fieldhouse Lane, Marlow, Bucks, SL7 1LS, UK. Email: matt.powell@osmose.co.uk

### INTRODUCTION

The Royal Process is a method for drying timber, which has been in commercial use for over 20 years (Wilkinson 1978, Richardson 1979, Borsholt 1983). Wet timber is heated in oil under vacuum. Water evaporates rapidly from the timber reducing the moisture content to a predetermined acceptable level, with the correct adjustment of the process. Other enhancements can be combined with this process, as will be outlined in this paper.

Osmose has a long standing commercial interest in this process, this has increased in recent years owing to the requirement for treated timber to be dry before leaving sawmills. The Osmose Royale Process is used to dry and impart performance enhancement to untreated wet, treated and even heat modified timber.

#### *The Royal Process*

The Royal Process was developed and patented by Bror Häger as a process for drying treated timber (Häger 1971, 1974, 1976, 1981, 1983a and 1983b). The basis of the process is that untreated wet timber or treated timber can be dried to an acceptable moisture content, rapidly, with minimal risk of adverse effects on the timber.

The wet timber is placed in a treatment vessel, which is then flooded with an oil having a relatively high boiling point, in the range of 150 - 400 °C. The oil is heated to 60 - 90 °C. At the same time a vacuum (-0.03 – -0.16 bar) is applied. The reduced pressure caused by the vacuum being drawn leads to a reduction of the boiling point of water. The boiling water in the timber evaporates away and is removed from the treatment vessel by the vacuum.

After sufficient water has been removed, the oil is pumped out of the treatment vessel. Once the treatment vessel is emptied of oil, a vacuum is drawn to remove excess oil from the surface. After surplus oil has been removed, the timber is taken from the treatment vessel and the treatment is complete. Depending upon the performance enhancement required, the process schedule can be modified to leave more oil in the timber.

Using the Royal Process treated timber is dried and ready to leave the site. There are other beneficial effects arising from the composition of the stabilising oil, any additives in the oil and the amount of oil deposited in the timber.

#### *Timescale*

Generally the period of drying for timber treated with the Royal Process will be of the order of 4 - 6 hours for timber of a thickness of 25 mm and 6 - 8 hours for 50 mm. This may be 25 - 50 times faster than conventional drying processes where air is the drying medium.

#### *Temperature*

The temperature of the stabilising oil needs careful consideration. There is a balance to be struck between the wish for as fast a drying process as possible and a requirement not to cause



damaging effects to the timber. By heating the oil to 60 - 90 °C the timber can be dried with minimal warping, cracks and tension.

**Hot Oil Treatment**

It is important to distinguish between the Royal Process and Oil Heat Treatment as developed by Menz Holz (Sailer 2000, Militz 2002). This latter process is where timber is heated in oil to temperatures of 180 – 220 °C. This higher temperature heat treatment causes chemical changes in the timber. This leads to improved durability of the timber against some fungi and improved dimensional stability, but at the expense of making the timber more brittle.

**Spacing**

When air drying timber there is a requirement for adequate spacing around all the timber pieces in order to facilitate good air circulation. This will lead to more efficient and consistent drying. In the Royal Process this is less of a concern as the wood is surrounded by oil with a high heat capacity. The oil is stirred by the escaping water vapour bubbles. This will lead to a uniform temperature in oil, subsequently leading to uniform heating of the timber. However there is a need for spacers when the oil is removed from the treatment vessel. This is to aid the drainage of oil from the timber.

**The Stabilising Oil**

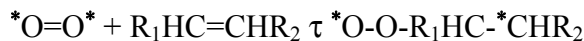
The nature of the stabilising oil used to dry the timber is obviously very important and the oils used in the Osrose Royale Process are carefully selected and blended to match the end use requirements. Depending on the oil or blend of oils, certain effects will be observed, which will ultimately affect the properties of the timber.

The stabilising oil always has a boiling point significantly greater than that of the water, so that evaporative loss is avoided. The boiling point can range from 150 - 400 °C. The stabilising oil can consist of drying oils, non drying oils, low boiling oils and high boiling oils, as discussed below.

**Drying Oils**

Certain fatty oils will form a dry, tough, durable surface film upon exposure to air. This is owing to their chemical make up. They contain a high proportion of unsaturated fatty acids, which will undergo oxidative polymerisation (Fieser 1961). These oils are used extensively in paints to form durable coatings.

The oxidative polymerisation is initiated by reaction of the unsaturated fatty acids' double bonds with oxygen in the air. This leads to polymerisation caused by free radical reactions of the reacted molecule with other carbon = carbon double bonds. A simplified reaction mechanism for this is shown in Figure 1.



*Figure 1: Oxidative Polymerisation.*

These oils are particularly beneficial when a hard surface is required. They often have a yellow colour. If a large enough proportion of drying oils to non-drying oils is used, then smearing and an oily feel on the surface of the timber can be avoided.

### ***Non-drying Oils***

These consist mostly of fully saturated oils. Hence there is little chance to undergo oxidative polymerisation. These oils will therefore remain fluid in the timber.

In general these oils have no strong odour. They are generally light in colour. However too high a proportion will lead to smearing and an oily feel on the surface of the timber.

### ***High Boiling Oils***

The high boiling oils have boiling points in the range of 300 – 400 °C. These consist of drying oils and non-drying oils, as described previously, which remain in the timber to impart performance enhancement, e.g. colour, surface protection. In order for the timber to gain these useful properties, the non-drying oils must exhibit low volatility, hence the need for a high boiling point.

Drying oils have less of a requirement for low volatility as they will polymerise in the timber and hence not evaporate. However, in the treatment plant, where vacuums are being drawn, low volatility of drying oils is still required.

### ***Low Boiling Oils***

The low boiling oils have low boiling points, in the range of 150 – 250 °C and low viscosity. They are present to help control the uptake of the high boiling oils.

High and low boiling oils and additives penetrate into the timber surface at the same time as a consequence of the temperatures and pressures of the process. A proportion of the low boiling oils, without other additives, will evaporate from the wood along with the water. After the heating oil has been removed from the treatment chamber, the rest of the low boiling oils evaporate owing to the vacuum. This will mean only the high boiling oils will remain in the timber, imparting performance enhancement. The proportion of the low boiling oils in the stabilising oil controls the uptake of high boiling oils and hence the properties of the treated timber.

The low boiling oils can be recovered by condensation of the fluids evaporated from the timber. This can be performed by attaching condensing equipment to the vacuum system. They can be subsequently separated from the condensed water and recycled.

Low boiling oils reduce the viscosity of the stabilising oil. Low boiling oils can thin fluids containing additives, which themselves increase the viscosity of the stabilising oil.

### ***The Effects of Stabilising Oil Composition***

Another aspect of the Royal Process is the tendency to withdraw resins from the timber. The withdrawal is greater with oils high in aromaticity. This obviously has the advantage of reducing or even eliminating resin bleed issues in painted timber.

The stabilising oil deposited in the timber by the Royal Process imparts water repellency, reducing water uptake (Treu 2001) and hence improved dimensional stability of timber.

A study has shown that mould growth on CCA treated timber was reduced by applying the Royal Process rather than kiln drying (Edlund 1985). There are two possible reasons for this effect. The more likely reason is the reduced uptake of water by the timber, which inhibits the growth of the mould. Mould growth is promoted by moisture. However oils that may be used in stabilising oils have exhibited minor inhibition of the growth of decay fungi (Paajanen 2002) and hence may have an effect on other types of fungi, such as mould.

Osmose stabilising oil is therefore formulated with consideration of the applications of the timber and the properties that are required.

#### ***Additives to the Stabilising Oil***

As mentioned previously there are additives that can be incorporated into the stabilising oil to impart the desired properties to the timber. These include additives to further enhance the water repellency, pigments and UV stabilisers for improved appearance of the timber and biocides to protect the timber. Each of these additives will now be considered.

#### ***Water Repellent Additives***

Although the Royale Process itself will impart some water repellency to the timber, this can be further improved by additives, as can be seen from the Osmose test results below.

Individual pieces of timber were dipped in stabilising oil, at 80 °C, containing additives and held submerged for 2 minutes. The pieces were then removed and allowed to dry for one day.

Once touch dry, the timbers were subjected to the sessile drop test in which one drop of water is placed on each piece of timber and the time taken to be absorbed into the surface indicates the water repellency of the timber. This procedure was repeated three times and the average time for absorption calculated.

***Table 1: Showing the time taken for water to be absorbed into the surface of treated timber.***

<b>Material concentration</b>	<b>Water absorption (seconds)</b>
Control (no additive)	37
1% additive 1	40
2% additive 1	68
4% additive 1	221
8% additive 1	> 300
Control (no additive)	59
1% additive 2	51
2% additive 2	100
4% additive 2	207
8% additive 2	198

Table 1 shows that the choice of additive and the level at which it is present is important. Of the two additives, additive 1 performs better. Increasing additive 2 above 4 % appears to have not effect on water absorption, but additive 1 continues to reduce water absorption further at a concentration of 8 %.

#### ***Pigments***

In addition to the finish provided by the stabilising oil, pigments can be added to enhance the decorative effect of the treated timber. Osmose supply oils containing yellow, red or brown pigments. These produce a durable coating which can maintain its colour for up to 6 - 10 years on cladding under average exposure conditions.

The appearance of the timber is enhanced and weathering of the timber is reduced by the addition of pigments to the stabilising oil. Evidence of this resistance is being observed in an outdoor decking trial set up in the UK.

### ***UV Stabilisers***

Ultra violet light affects the appearance of timber, causing the colour to fade to grey and making the surface of the timber more friable. This colour fade can be accelerated by the initial treatment process, e.g. heat treatment. The addition of UV stabilisers to the stabilising oil can help delay colour fade and hence prolong the original appearance of the timber.

### ***Biocides***

Where there is the need to improve the protection offered by the stabilising oil treatment it may be desirable to add an appropriate biocide to the oil formulation. These biocides must be heat resistant, chemically stable in the oil and also stable in contact with water. Heating to 90 °C and exposing to steam can be a severe challenge to the chemical stability of many biocides. The biocide will only be deposited where the oil penetrates and so may be very superficially applied when low levels of stabilising oil are present.

### ***Overpainting***

Unpigmented stabilising oil can be considered as a primer for the timber. As has already been mentioned resins can be withdrawn from the timber by the stabilising oil. This improves the overpaintability of the timber, as subsequent resin bleed will be reduced in timber that is prone to such problems.

Testing has also shown that timber treated with Royale stabilising oil can be overpainted with a first coat of certain paints in as little as 14 hours after treatment. This timescale for overpainting timber treated with Royale stabilising oil may however be affected by the specific paint chemistry.

Royale stabilising oil was applied to timber using the following treatment schedule: 5 minutes of -0.8 bar vacuum, 5 minutes of immersion at 0.3 bar pressure with stabilising oil at 80°C and 20 minutes of -0.8 bar vacuum. After treatment the samples were stacked in various configurations, either with treated faces touching or separated by stickering with timber, for various lengths of time prior to coating.

The coating material was applied by dipping for 30 seconds. Two coats were applied 4 hours apart, and the samples were then dried for seven days on the laboratory bench.

The coating was removed from one face of each sample by power planing. Samples were then placed coated face up for 50 hours over a steam box, running with a water temperature of 50°C.

After 50 hours on the steam bath, samples were removed and 'cross hatch' tested within an hour of removal, using an 8 x 8 cross hatch cutter to produce 2mm by 2mm squares and a pull of tape firmly applied to the coated surface. The number of squares of coating adhering to the tape (i.e. removed from the timber) was recorded.

**Table 2: Effect of drying conditions on extent of coating removal after 50 hours over a steam box.**

Drying Time	Test face orientation on drying		Squares Removed
	Touching	Separated by stickers	
14	✓		0
14	✓		0
14		✓	0
14		✓	0
24	✓		0
24	✓		0
24		✓	0
24		✓	0
64		✓	0
64		✓	0

***Timber Enhancement with Osmose Stabilising Oil.***

Royale stabilising oil can be used to supplement timber treated by other methods to control against wood destroying organisms. The following is an overview of some of the treatments that Osmose stabilising oil can complement and an indication of the issues that need to be addressed with each system.

***Copper Containing Aqueous Fluids***

Care needs to be taken with copper containing fluids as they can degrade the stabilising oil, reacting with the unsaturated drying oils. The Osmose Royale system has been designed to eliminate this problem.

***Heat Treated***

It may not be immediately obvious why heat treated timber will require treatment with stabilising oil. The timber has already been subjected to temperatures and timing in excess of the Royale Process and hence is dry. It has also gained dimensional stability owing to the chemical changes caused by the heat. The timber may even have gained a brown colour, depending on the treatment temperature and time.

However, heat treated timber exhibits rapid colour fade on exposure to UV light (Jämsä 2000). Therefore a treatment involving a stabilising oil containing UV stabilisers and/or pigments can lead to a more durable, attractive appearance to the timber.

Heat treated timber also becomes brittle (Vernois 2000), again depending on the treatment and time. A hardened, protected surface imparted by the stabilising oil will lead to a less friable surface.

***Untreated Damp Timber***

Untreated damp timber can be dried by stabilising oil. To impart some protection against wood destroying organisms, biocides can also be included. By this method timber can be protected by the stabilising oil alone, without the requirement for other treatments. This can only be applied to situations where a superficial treatment with biocides is sufficient for wood protection.

## CONCLUSIONS

This paper has outlined the Osmose Royale Process and the benefits of incorporating Osmose stabilising oil into the surface of timber. The timber gains performance enhancement in the form of water repellency and dimensional stability. Additives lead to improved weathering, water repellency and protection against biodeterioration. Timber impregnated with wood preservatives and treated with the Osmose Royale Process can leave sawmills in much less time than if air dried. Osmose stabilising oil can supplement or even substitute for other timber protection processes.

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## A Study of Water Loss and Oil Absorption during Oleothermic Treatment of Wood

D.Grenier<sup>1</sup>, H.Baillères<sup>2</sup>, J-M.Méot<sup>3</sup>, P.Langbour<sup>4</sup>, J-D.Lanvin<sup>5</sup>

<sup>1</sup> CIRAD, TA 10/16, Avenue Agropolis, 34398 Montpellier cedex 5, France, david.grenier@oreka.com

<sup>2</sup> CIRAD, TA 10/16, Avenue Agropolis, 34398 Montpellier cedex 5, France, henri.bailleres@cirad.fr

<sup>3</sup> CIRAD, TA 10/15, Avenue Agropolis, 34398 Montpellier cedex 5, France, jean-michel.meot@cirad.fr

<sup>4</sup> CIRAD, TA 10/16, Avenue Agropolis, 34398 Montpellier cedex 5, France, patrick.langbour@cirad.fr

<sup>5</sup> CTBA, Allée de Boutaut BP 227, 33028 Bordeaux cedex, France, jean-denis.lanvin@ctba.fr

**Keywords:** treatment, process, oleothermic, oil, wood

### ABSTRACT

Currently, Cirad manages the research and development of a process for oleothermic treatment of wood using two stages (Patent PCT/FR 00/03245). In order to determine the optimum treatment conditions for different species and geometries, process engineering methods, rather than tests on commercial sized samples have been used. The presented work is aimed at observing the conditions under which the wood is subjected to during the process and what are their consequences. During heating, the inside of parallelepiped samples (16 cm x 5 cm x 3 cm) from beech (*Fagus sylvatica*) in which the water content is 110% of dry weight, reach temperatures around 100°C, with the pressure increasing up to values close to 3 absolute bars. Tests at different temperatures on samples with closed ends in fibre direction, reveal a dependence of the drying and the impregnation rates, according to the temperature. To conclude, during the wood characterisation with a view of defining the treatment conditions with this process, we must attach importance to the temperature between 100 and 120°C and use differences of pressure between sample faces around 1 and 3 bars. At the time that we will obtain the values in these conditions, we must wonder what possibility to correlate with the existing values taking from the drying studies.

### INTRODUCTION

This process can be divided into two phases.

The first phase consists of submerging the wooden piece into an oil bath at 160°C – 200°C. In the presence of strong heat flows, the material warms up to over 100°C. The water, which is contained in the cells, evaporates creating an overpressure inside the wood. This vapourisation moves from the surface to the centre. There is a steam repulsion outside the wooden piece, mostly in the fibre direction. In the second phase, the wood piece is soaked into an oil bath at a temperature lower than the boiling temperature of water, at the pressure in the cold bath.

The wooden piece then cools down leading to water condensation. The created low pressure causes oil penetration. This process has a number of advantages which are the following:

- A fast dryer, with a high thermal efficiency and without high damages of the material
- The possibility to use oils and thermosensitive products for impregnation
- The ease of use of the equipment



Within the context of this process study, several studies were carried out. The study presented concerns the method to determine the application conditions of the process to one wood species and one geometry only. The way how to do consists in determining firstly, on samples, the characteristics of transfer. Then, using empirical rules or knowledge, the extrapolation to real pieces to give the start conditions for an experimental optimisation.

We have looked for determine the conditions to which the material is subjected during the process. This knowledge is necessary to develop new adapted methods of measurement of transfer characteristics.

An initial experimental set shows that the inside of wooden pieces is subjected to pressures around 3 absolute bars. A second set lets appeared a non linear behaviour of wood beside the temperature.

## EXPERIMENTAL METHODS

### *Samples*

Tests have been carrying out using beech (*Fagus sylvatica*). Parallelepipeds of dimensions 16x5x3cm were prepared, the biggest length being chosen in the fibre direction. Samples were rehydrated before testing by cold soaking in an autoclave under pressure for 2 days. Their water content was between 105 and 120% DB (Dry Basis).

### *Simulation of pieces in full size*

For some experiments, a simulation of phenomena occurring in the centre of full size pieces, was obtained by closing the ends of the samples. As shown in figure 1, a metal stirrup applies under pressure a silicone sheet to each end. During the tests, the non production of steam bubbles at the ends validates this device efficiency.



*Figure 1: Presentation of the sample in the stirrup*

***Oils used for the experimental tests***

The results presented in the following document, have been obtained using the following oils :

- Hot bath: Groundnut oil
- Cold bath: Linseed raw oil (cold squeezed)

The groundnut oil was chosen for its resistance qualities at high temperatures and its availability. Naturally, in an industrial application case, a cheaper oil can be used.

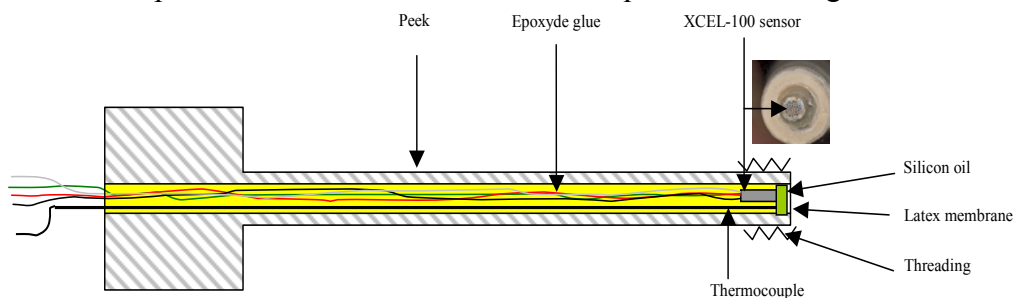
***Heater and cooler baths***

For the tests, a stainless steel container of dimensions 30x15x15 cm was used as the hot bath heated by a submerged electric resistance heater of 2 kW. Three thermocouples were cabled in parallel to obtain an indication of the average oil temperature in the container. A PID control allowed for temperature regulation, which limited fluctuations by +/- 2°C around the target value. The cold bath was a stainless steel container similar to the one used for the hot container.

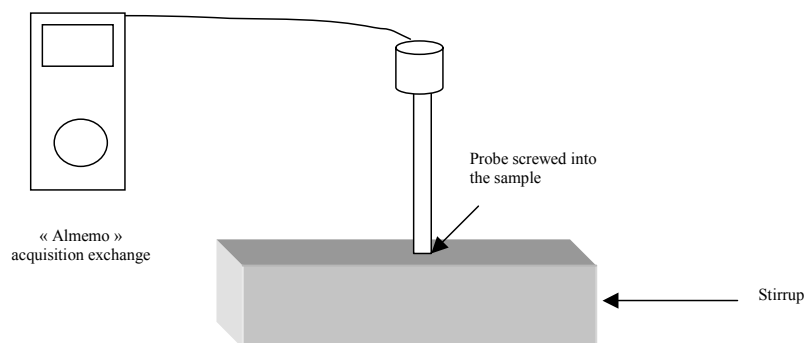
***Pressure and temperature measurements inside samples***

The pressure was measured by a sensor KULITE XCEL-100 (Range 0 – 7 absolute bars) of 3 mm in diameter, compensated by 25°C up to 232°C. This sensor and a thermocouple was linked together with an epoxy glue inside a Peek tube. The overall diameter of the tube was 8 mm. The outside of the tube was threaded in order to permit a watertight seal of the device into the wood. These sensors are protected at their end by a thin silicone oil film covered by a latex membrane (Fig. 2).

The probe was screwed into the previously threaded sample (Fig. 3). The acquisition values of pressure and temperature were carried out with an acquisition exchange "Almemo".



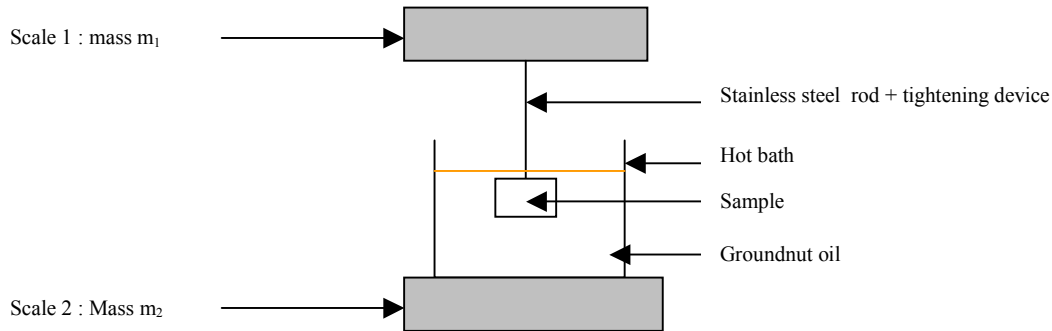
***Figure 2: Assembly of the pressure sensor and the thermocouple in the Peek probe***



***Figure 3: Experimental device for measuring simultaneously temperature and pressure inside the sample.***

**Monitoring of oil and water contents during heating**

In the hot bath, samples as described in point 1, were weighed by two scales. (Fig. 4).



**Figure 4: Experimental device of double weights**

The heater container was put on one scale. The sample is linked by a mechanical tightening device hanging under the second scale above, by a stainless steel rod of 1 mm in diameter. This experimental device has been developed and used by Olivier Vitrac during his doctorate (Vitrac 2000).

The weights measured by the scales are as follows :

Weight m1 : Visible value from the scale under the hot bath.

$$(1) m_2 = m_{\text{hot bath}} + m_{\text{oil into the hot bath}} + m_{\text{oil removed by the sample}} + m_{\text{oil removed by the tightening device}} + m_{\text{oil removed by the steam bubbles hanged to the wood piece}}$$

Weight m2 : Visible value from the scale holding up the sample

$$(2) m_2 = m_{\text{ml}} + m_{\text{oil into the sample}} + m_{\text{water into the sample}} + m_{\text{tightening device}} - m_{\text{oil removed by the sample}} - m_{\text{oil removed by the tightening device}} - m_{\text{oil removed by the steam bubbles hanged to the wood piece}}$$

We obtain by calculation

$$\Delta m_{\text{oil into the sample}} = -\Delta m_1 + \Delta m_{\text{oil removed by the sample}}$$

$$\Delta m_{\text{water into the sample}} = \Delta m_1 + \Delta m_2$$

These calculations are possible subject to the following hypothesis :

- The weight of ligneous matter (ml) doesn't change during heating.
- The volume weight of the removed oil by the tightening device remains constant.
- Oil is not removed by vapourisation during heating. This has been experimentally verified by heating the oil up to 180°C for 3 hours.
- The influence of steam bubbles located under the sample is negligible. This hypothesis probably brings about an overestimation of the eliminated water quantity and of the oil quantity into the sample. Some tests by indicate that the eliminated water error is around 14% of the dry weight for heating at 180°C, extreme cases of our tests.
- The sample is subjected to the same volume variations according to the moisture, whatever the temperature of the hot bath.

***Oil Penetration during soaking***

The monitoring of the oil penetration during soaking in a cold bath was done by a device with two scales similar to the one used to quantify transfers into the hot bath. The measured weights are similar to the ones obtained on the hot device, considering that there are no more bubbles ( $m_{\text{oil removed by the steam bubbles hanged to the wood piece}} = 0$ ).

So,

$$\Delta m_2 = - \Delta m_{\text{oil into the sample}}$$

$$\Delta m_1 = \Delta m_{\text{oil into the sample}}$$

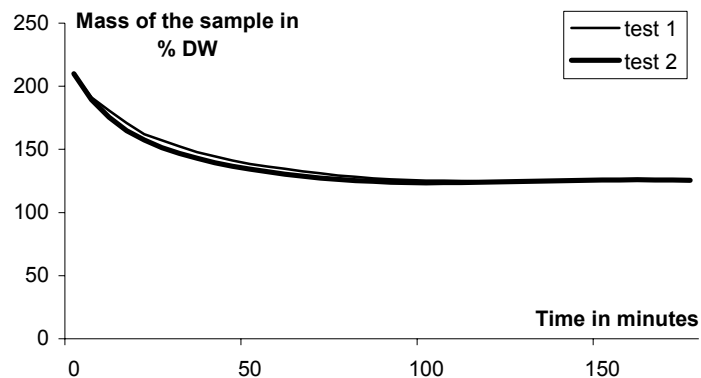
In addition to the previous hypothesis, we must add :

- Water doesn't evacuate during soaking.
- The oil weight removed by the sample remains constant during soaking.

***Tests repetition***

At the end of the methods and apparatus development, a test at 150°C on samples with opened ends was repeated 4 times. The results gave a very good repeatability (Fig. 5). Afterwards, each test was run once.

Note : Afterwards, weights are expressed in % of the dry wood weight without taking into account the oil weight of the material (% DW).



**Figure 5: Example of repeatability ; Monitoring of weight of two samples heated at 180°C**

## RESULTS AND DISCUSSION

***Pressure and temperature measurements during heating to 180°C then soaking***

During the first minutes of the heating, the pressure increases into the sample with closed ends (Fig. 6). The pressure is maximal when the temperature reaches 110°C (2.7 absolute bars). The pressure then falls slowly to close to atmospheric pressure. We noticed a slight temperature decrease. When all the water is almost outside of the sample, the temperature increases again. The sample is then soaked into a linseed oil bath at the initial ambient temperature (20°C). The pressure falls suddenly to reach 0.25 absolute bars. Then the pressure increases up to the atmospheric pressure and the temperature falls down to reach the equilibrium temperature of the bath and sample. The curves correspond to the ones obtained by Olivier Vitrac during his measures on samples of frost (Vitrac 2000).

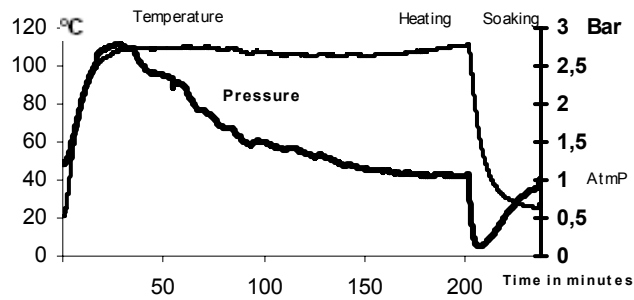


Figure 6: Simultaneous measure of the absolute pressure and of the temperature inside the beech parallelepiped sample (16\*5\*3 cm) with closed ends.

**Water end oil transfers during heating at 120, 150 et 180°C on samples with opened ends**

As shown in figure 7, water comes out of the sample faster as the oil bath temperature is increased. After 3 hours of treatment, the heated sample at 180°C lost 7%DW more than the one heated at 150°C and 22%DW more than the one at 120°C.

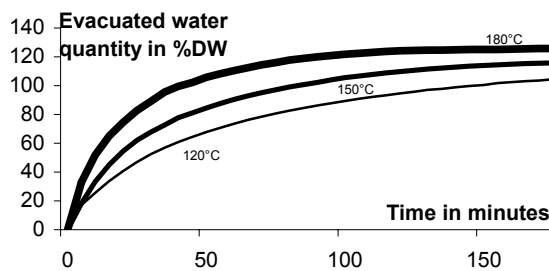


Figure 7: Comparison of the evacuated water quantity during heating on samples with opened ends at 120, 150 and 180°C

The monitoring of the oil penetration (Fig. 8) during soaking into the hot bath of samples with opened ends, exhibits a correlation between the water lost and the oil gained (Fig. 9).

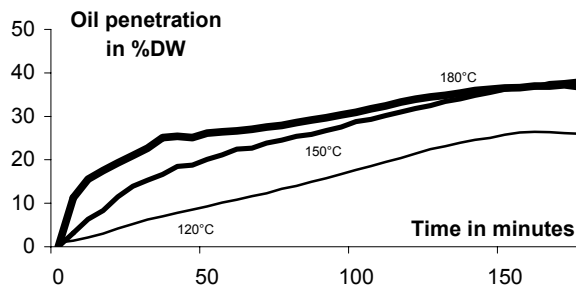
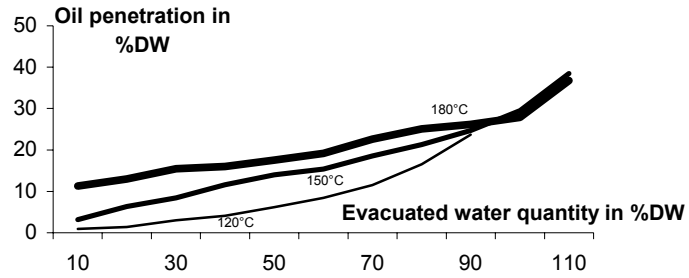


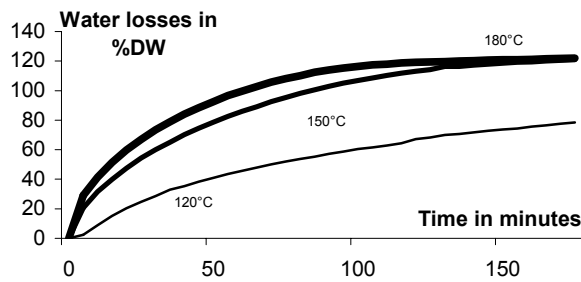
Figure 8: Comparison of the oil penetration into samples during heating at 120, 150 and 180°C



*Figure 9: Comparison of the oil penetration into samples during heating at 120, 150 and 180°C ; plotted function of the evacuated water quantity*

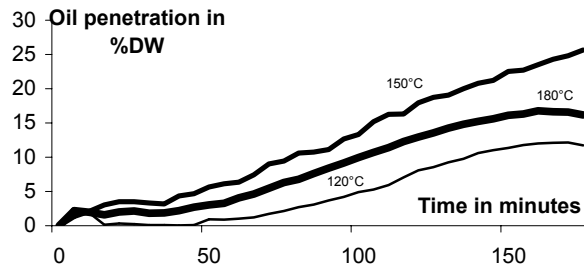
**Water end oil transfers during heating at 120, 150 et 180°C on samples with closed ends**

Figure 10 presents the observed water losses during heating at 120, 150 and 180 °C on samples with closed ends.



*Figure 10: Water losses of samples with closed ends during soaking in hot bath*

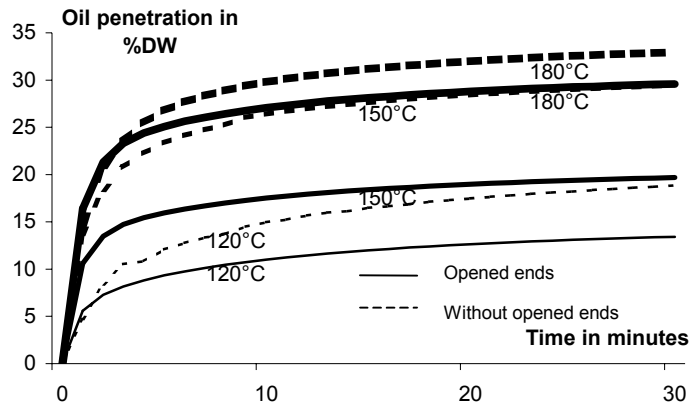
When the ends are blocked, the oil gains, after 3 hours of heating, are between 12 and 22% DW according to the temperature. We found that the oil gain was greater at 150°C (22%) than at 180°C (15%) (Fig. 11).



*Figure 11: Comparison of the oil penetration into samples during heating at 120, 150 and 180°C (Tests at 150°C and at 180°C repeated twice), closed ends*

***Linseed oil penetration during soaking in cold bath***

During soaking at 30% of the residual moisture at the heating end, the oil of the soaking bath penetrates the wood even better, since the temperature of the heating bath is high (Fig. 12). This difference decreases between 180 and 150°C when the ends are blocked. 90% of the oil gain occurs in the first 5 minutes. This oil gain corresponds to the phase of an important depression into the wood.



**Figure 12: Comparison of oil gains between samples with or without opened ends treated at different temperatures in hot bath, during soaking in cold bath**

## DISCUSSION

The monitoring of the temperature and of the internal pressure during soaking in the hot bath reveals a high rise of pressure inside the samples. This pressure isn't only due to the water vapourisation, since the measured temperatures are relatively low. In the given example, the internal temperature would have to be around 131°C in order to obtain an equilibrium water – steam and so, an absolute pressure of 2.8 bars.

The presence of internal pressure can induce changes in the wood behaviour with respect to weight transfers. On samples with closed ends, the more important gain of oil, noticed during heating in a bath at 150°C, in comparison with heating baths at 120 and 180°C seems to indicate that, in certain conditions of pressure gradient and water content, the permeability can be increased. The phenomenon is less clear with the water loss but the obtained kinetics, during heating at 150°C and at 180°C appear to be coherent with this logic.

At the time of the double weight, the observation of the sample (bubbles forming) during heating reveals that the watertight seal due to the metallic stirrup holds during all the experimental time. The repeatability was verified on samples heated at 150°C and 180°C. During the experiments, we consider that the sapwood of the beech has almost the same behaviour as the heartwood. The obtained results don't reveal significant aberrations.

Ring orientation of the wood, does not result in any significant changes of the oil penetration (weak transversal shooting).

The uncertainty of the influence of the presence bubbles in the oil and under the sample during the double weight, leads to an overvaluation of the oil quantity truly inside and of the evacuated water.

The oil absorption is slightly more after 3 hours heating for a sample heated at 150°C than for a sample heated at 180°C (2% more of dry weight). This phenomenon is more marked for samples with closed ends (7% more of dry weight). This last result reveals the complexity of weight and heat transfers during the process. We have to wonder about the pertinence of the characteristics to measure with a view to piloting the industrial process.

To be interpreting, this work has to take into account the water repartition into wood during heating. On the other hand, we may notice that this work was with a specific species and so, all extrapolation to others species must be carried out with caution.

## CONCLUSIONS

The measure of pressure, sample with closed ends, confirms the presence of an internal pressure in the wood during heating and a low pressure during soaking. The oil entry into samples with opened ends during heating (3 hours) is roughly 25% - 35% of dry weight. This oil quantity depends of the moisture content of the sample and on the heating temperature. The oil entry into samples with closed ends during heating is at least half that into samples with opened ends (10% - 20%). The absorbed oil quantity during soaking occurs at 90% in the first 5 minutes. The oil quantity taking by samples simulating the central part of the pieces in full size is 30% of the dry weight. This quantity is slightly more important (<5%) than for the samples simulating ends. Leaving the sample 24 hours more in soaking results in a 5% increasing of oil uptake when the ends are opened and a 3% increase when the ends are closed (% of dry weight). This method of heating and soaking permits, from a wood with a 110% initial moisture, to have 32% of oil penetrated in around half an hour. A dry sample (11 - 12%) only soaked into oil at ambient temperature takes 20% of oil in 2 days (opened ends).

Note: The bibliography quoted here does not solely refer to references in the text.

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## Post-Treatment of Thermo-Hydro-Mechanical Densified Wood with a New Multiparameter Reactor

Frédéric Heger<sup>1</sup>, Fred Girardet<sup>2</sup> and Parviz Navi<sup>1</sup>

<sup>1</sup>Laboratory of Building Materials, Swiss Federal Institute of Technology, Lausanne, Switzerland

<sup>2</sup>Expert Center – For Conservation of Cultural Heritage, Lausanne, Switzerland

**Keywords:** Thermo-Hydro-Mechanical densification, recovery, post-treatment, permanent fixation

### ABSTRACT

Wood has a tubular microstructure with polymeric constituents. In addition, under high temperature ( $> 90^{\circ}\text{C}$ ) and saturated vapour conditions wood becomes plastic. Thanks to these two properties, wood can be easily densified in its transverse direction in order to reduce its porosity or deformed to give a new shape. The result of the densification is a new material with much higher mechanical properties, especially the shear stress strength and hardness. Unfortunately, the densified state is metastable. For instance, when densified wood is soaked in hot water, it recovers its initial shape. The recovery percentage depends on the densification conditions (i.e. temperature, compression rate or water content). We have shown that through THM post-treatments one can stabilise totally the densified shape. A new multiparameter reactor has been constructed in order to densify and to post-treat samples in the same chamber under different conditions (temperature up to  $200^{\circ}\text{C}$ , duration, relative humidity, pH, inert gas). It is commonly admitted that the densified wood recovery is due to the inner stress accumulated during the densification. So the elimination of this recovery would be due to the release of the inner stress or to the forming of strong new bonds between the densified wood components during post-treatments. However, there is no satisfying explanation at the macromolecular level. In this context, hydrolysis of the polysaccharides,  $T_g$  of the lignin or number of sorption groups ( $-\text{OH}$ ) seem to be determining factors. Thus chemical and physical analysis (DSC, GPC analysis, total hydrolysis, sorption isotherms) have been carried out to understand the chemical and macromolecular modifications of cellulose, hemicelluloses and lignin during densification and post-treatments. Mechanical properties such as the shear stress resistance and the Brinell hardness have been tested to measure the improvement of mechanical resistance.

### INTRODUCTION

In Navi and Girardet (2000), small wood specimens of different species were densified using Thermo-Hydro-Mechanical (THM) actions in a closed system. The complete fixation of the transformed shape under compression was obtained using saturated steam at  $150^{\circ}\text{C}$ . Although the treated samples showed significant improvement in mechanical and physical properties with reduction in hygroscopic behaviour, the processing time for complete fixation of transformed shape was quite long (about several hours). Inoue *et al.* (1993) and Ito *et al.* (1998a,b) used higher steaming treatments at  $200^{\circ}\text{C}$  and needed only three minutes of processing time to obtain permanent fixation for sugi specimens of 15 cm diameter. It was postulated that steaming treatment hydrolyses partially the paracrystalline region of cellulose and hemicelluloses, increased the cellulose crystallinity index (CrI) and microfibrillar width and decreased the length of cellulose microfibrils. Higher temperature steaming treatments (up to  $200^{\circ}\text{C}$ ) might transform the crystalline phase of cellulose from phase  $I_{\alpha}$  to  $I_{\beta}$  (Tanahashi *et al.* 1989a, Ito *et al.* 1998a).

Their results could explain the permanent fixation mechanism of densified wood with high temperature steaming (up to 200°C), but it might be no transformation under this temperature. Reduction of the post-treatment time from several hours to few minutes to obtain permanent fixation would obviously have a strong impact on the wood technology and on its valorisation. It is important to note that, in this process the role of water on the fixation of compressive set is fundamental. Water at high temperature not only participates in the chemical modification of the wood constituents to release the inner stress stored in compressed wood, but also considerably increases the kinetics of transformations during process.

Recently, we have studied the problems of fixation of THM densified wood by steaming at maximum 200°C. The densification and the post-treatment of wood were carried out in a new multiparameter reactor developed for this purpose. In this work the effect of post-treatment conditions, temperature and processing time, on the fixation of the compressive set were studied. The recovery of post-treated samples was measured using soaking-drying cycles. Transversal micrographs were made by confocal microscope to visualise the effect of post-treatments on recovery of compression set. In the following, after an explanation of THM wood densification and high temperature steam post-treatment, a brief description of the reactor is given. The results obtained from the set-recovery, the shear stress resistance and the Brinell hardness tests, as well as the sorption isotherms and the chemical analysis are reported. Our remarks are given in the discussion and conclusion part.

## EXPERIMENTAL METHODS AND RESULTS

### *THM Densification*

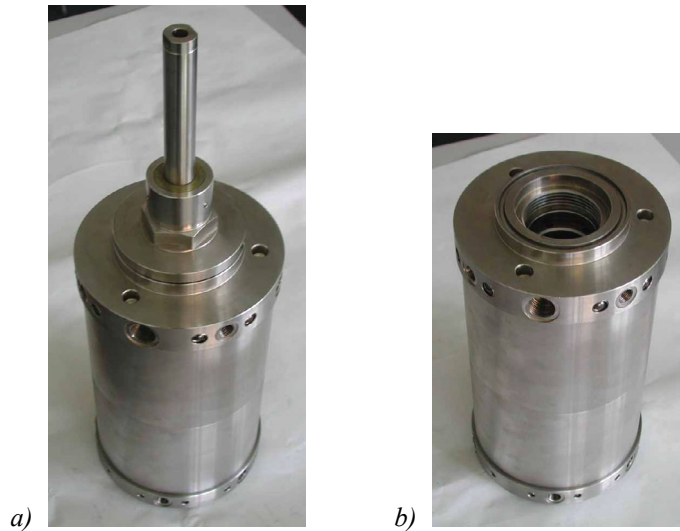
Small cylindrical specimens of spruce with 40 mm in diameter and 50 mm height were densified in radial direction under saturated steam in a multiparameter reactor (Fig. 1) under controlled displacement mode. The value of the compression set ( $C$ ) is defined as :

$$C = \frac{R_o - R_c}{R_o} \times 100 (\%) \quad (1)$$

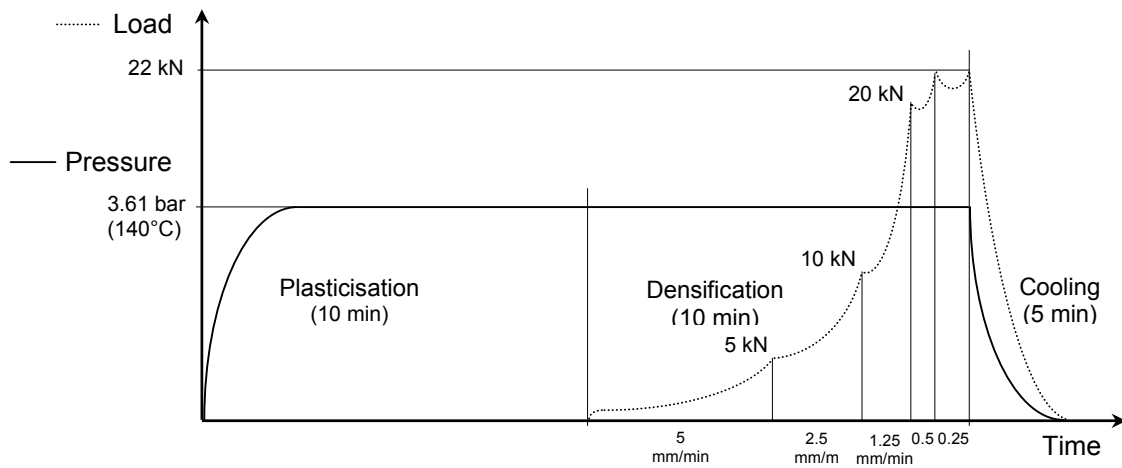
where  $R_o$  and  $R_c$  are the thickness of the samples before and after compression respectively. The value of the compression set varies between 60.6 and 71.7% depending on the initial density. A diagram of the THM densification procedure is given in Fig. 2. It consists in two steps : at first the sample is steam heated until 140°C (plasticisation) and then densified under controlled displacement mode at 5 mm/min until 5 kN, 2.5 mm/min until 10 kN, 1.25 mm/min until 20 kN, 0.5 mm/min until 22 kN and finally at 0.25 mm/min until 22 kN. When 22 kN is reached for the second time the piston is stopped. Then the sample is immediately cooled under 60°C in order to be removed from the reactor if the sample is not post-treated.

### *Post-treatment*

After densification, the samples have been post-treated in different conditions. Table 1 shows the conditions of the different post-treatments. As the post-treatments have been carried out under saturated steam, the temperature of post-treatment was easily controlled by pressure. After densification the piston was stopped and maintained in the same position during the whole duration of post-treatment. At the end of post-treatment the reactor was purged, the sample immediately cooled under 60°C and removed from the reactor.



**Figure 1:** a) Overview of the THM machine  
 b) Overview of the THM machine without piston and small removable cover



**Figure 2:** Diagram of the THM densification procedure

**Table 1: Temperature and duration conditions of post-treatments**

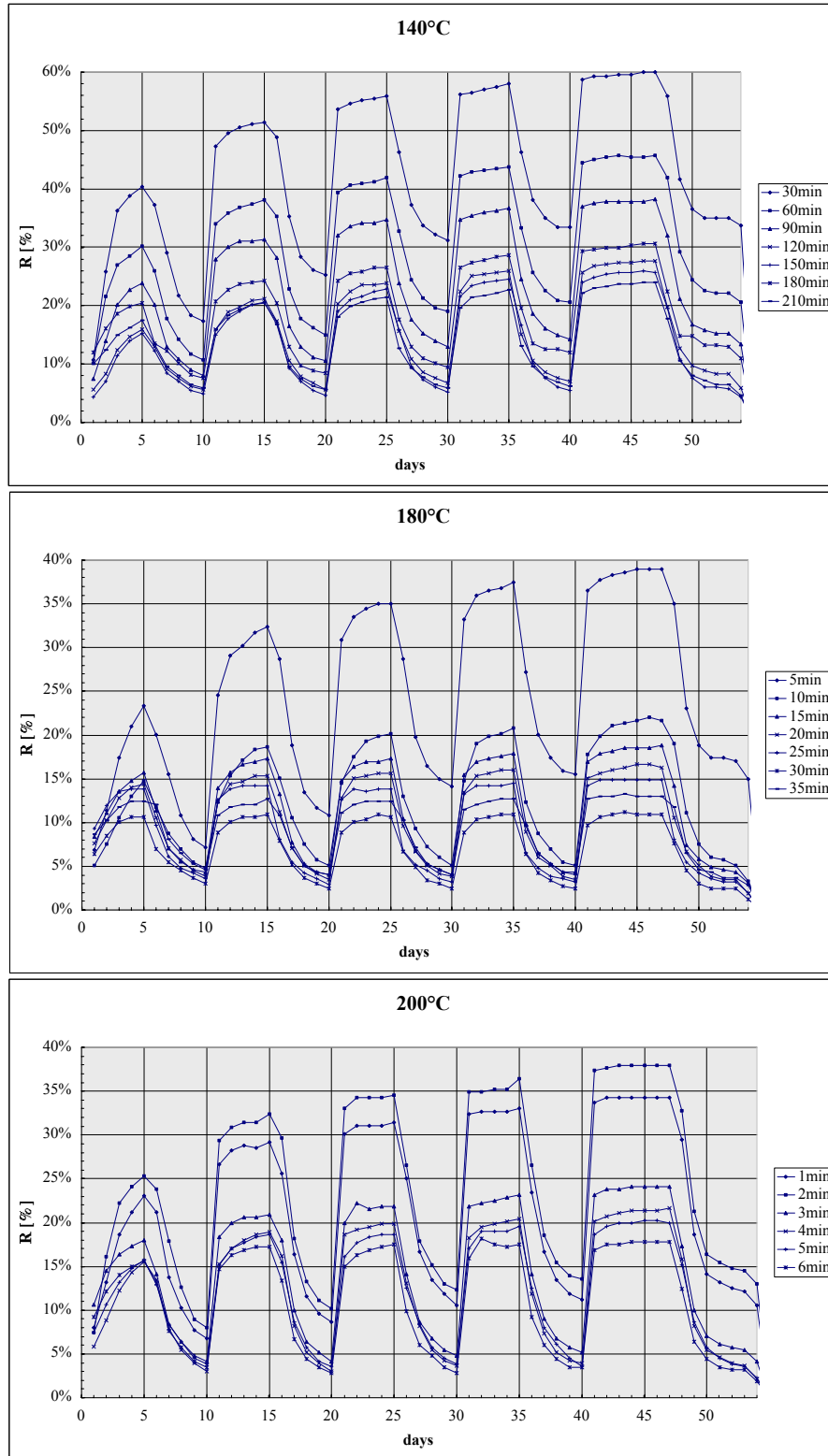
	Temperature						
	140°C	150°C	160°C	170°C	180°C	190°C	200°C
Post-Treatment Duration [min]	30	20	15	10	5	2	1
	60	40	30	20	10	6	2
	90	60	45	30	15	10	3
	120	80	60	40	20	13	4
	150	100	75	50	25	15	5
	180	120	90	60	30	18	6
	210	140		70	35		

**Set-recovery test**

In order to examine the effect of different THM post-treatments on recovery of compressive transformed shape, a set-recovery test was conducted on each sample. It consists in five soaking-drying cycles (1 cycle = 5 days in distilled water at 60°C followed by 5 day oven-drying at 30°C). During this test the recovered thickness ( $R_c$ ) was measured and the set-recovery (R) was calculated from the equation 2.

$$R = \frac{R'_c - R_c}{R_o - R_c} \times 100 \text{ (\%)} \quad (2)$$

After the fourth cycle, the samples were put into distilled water at 60°C during 7 days, then oven-dried at 30°C for six days and finally oven-dried at 60°C for two more days under primary vacuum.



**Figure 3a-e: Hydal behaviour of non post-treated and post-treated samples during soaking-drying cycles. The samples were treated at 140°C, 180°C and 200°C with different processing times**

The hydral behaviour of the specimens post-treated under different steaming temperature and processing time is given in Fig. 3a-e.

### ***Shear stress resistance tests***

Shear stress resistance tests have been carried out on three densified spruce samples. These samples had a squared section ( $c = 30$  mm,  $h = 40$  mm). The load has been longitudinally and parallel to the fibers axis. Table 2 gives the values of this test.

***Table 2: Shear stress resistance of non densified and densified spruce sample***

Spruce	Shear stress resistance [N/mm <sup>2</sup> ]
<b>non densified samples</b>	<b>4.7 - 12.0</b>
1st densified sample	121.4
2nd densified sample	107.2
3rd densified sample	103.4
<b>mean value</b>	<b>110.6</b>

### ***Brinell hardness tests***

The decrease of the porosity during the densification process makes the wood much harder in the radial and tangential directions. In order to measure the increase of hardness in these directions Brinell hardness (BH) tests have been carried out on spruce samples. Table 3 gives the results of this hardness test.

***Table 3: Brinell hardness of natural and densified spruce samples***

Spruce	tangential BH [N/mm <sup>2</sup> ]	radial BH [N/mm <sup>2</sup> ]
non densified samples	12	12
1st densified sample	70.8	71.3
2nd densified sample	52.8	59.8

### ***Sorption isotherms***

Thermo-hydric treatments are well known to decrease the hygroscopy of wood. Sorption isotherms have been carried out in order to quantify the absorption. The samples have been cut in thin chips. The following samples were used :

- 1 natural wood sample
- 1 densified wood sample
- 1 densified wood sample post-treated during 3 hours at 140°C
- 1 densified wood sample post-treated during 16 min at 180°C
- 1 densified wood sample post-treated during 4 min at 200°C

The results of these sorption isotherms are presented in Fig.4. By using the Dent sorption isotherm model, we have calculated the influence of post-treatment on the variation of –OH sites.

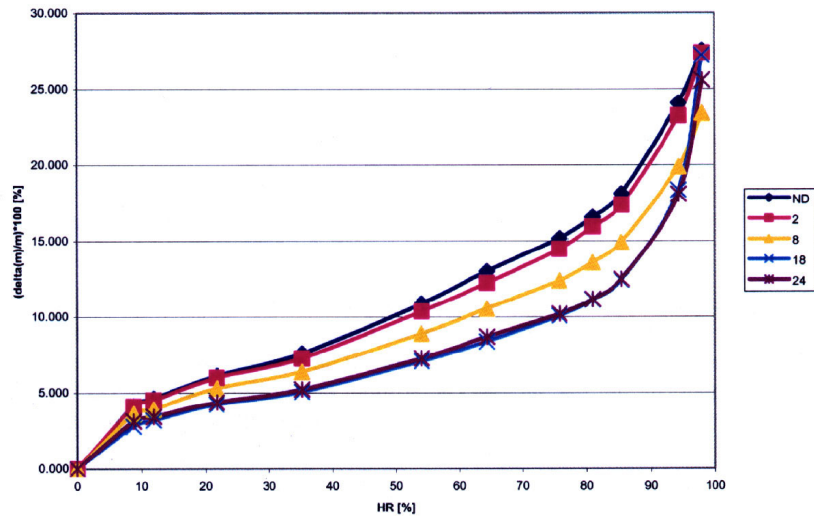


Figure 4: sorption isotherms. ND: natural wood, 2: densified wood, 8: densified and 140°C, 3 hrs post-treated wood, 18: densified and 180°C, 16 min post-treated wood, 24: densified and 200°C, 4 min post-treated wood

#### Gas Phase Chromatography (GPC) of polysaccharides

During the post-treatments, especially at 200°C, the acidic conditions change. As a matter of fact the pH of water at 200°C is not 7 but 6 and acetic acid is produced during post-treatments. In these conditions there is every chance that hemicelluloses are hydrolysed and dissolved in water. The neutral monosaccharides (glucose, galactose, mannose, xylose and arabinose) can be identified and quantified by GPC. Fig. 5 shows the GPC spectra of 3 samples. The chromatographs are referenced by an internal standard (inositol).

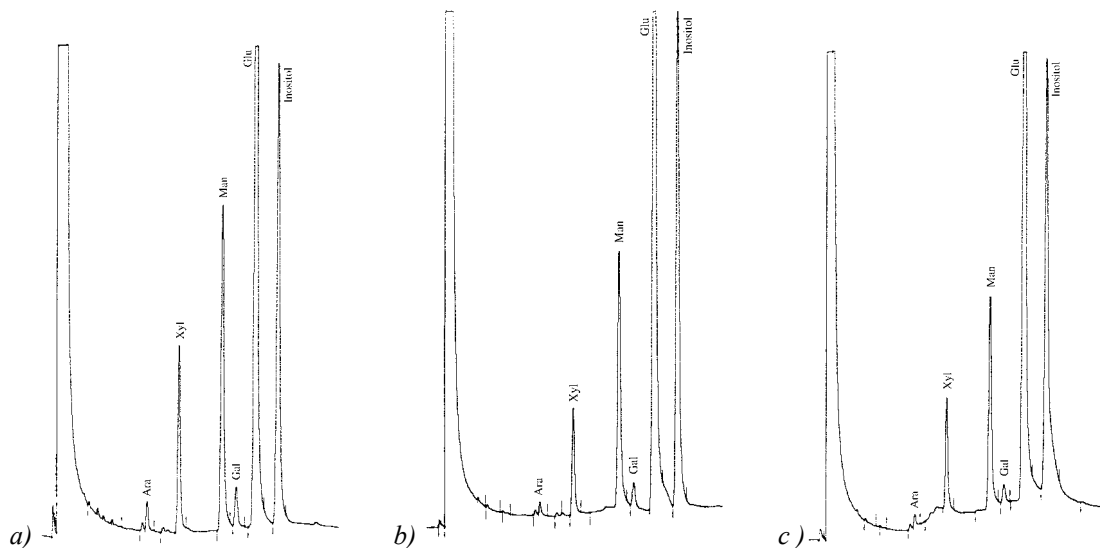


Figure 5: GPC spectra of monosaccharides. a) densified wood, b) densified and 180°C, 30min post-treated wood, c) densified and 200°C, 5 min post-treated wood

#### Glass transition temperature ( $T_g$ ) of lignin

As the lignin is a tridimensional reticulated amorphous polymer, its degree of reticulation and its  $T_g$  can vary during thermo-hydric treatments. So this temperature has been measured by DSC

between -30 and 240°C for several post-treated samples. Fig. 6 presents the  $T_g$  values depending on the temperature of post-treatment and its duration.

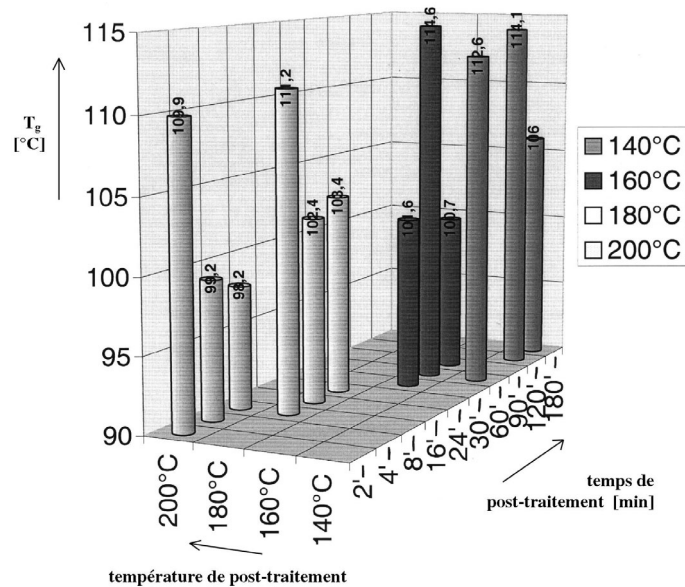


Figure 6:  $T_g$  of lignin after post-treatment

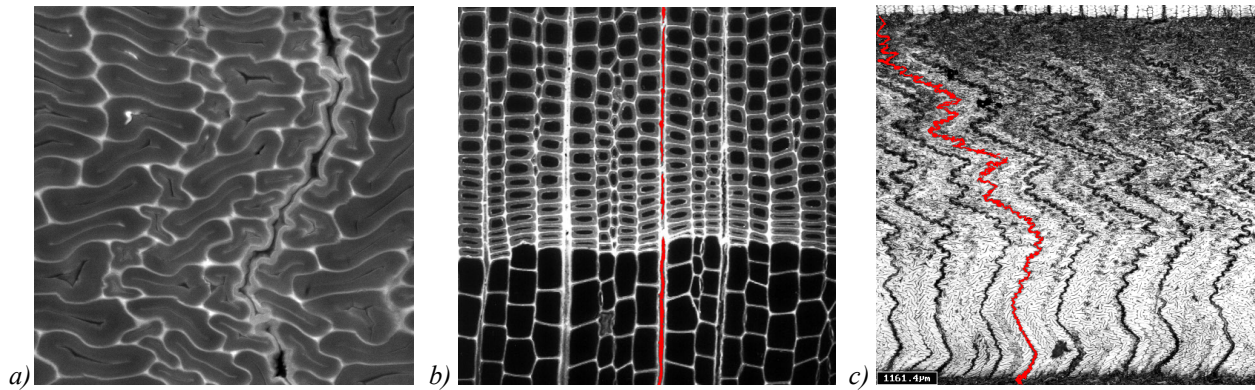
## DISCUSSION AND CONCLUSION

The density of spruce samples after densification was approximately tripled and the mean density of 24 specimens was 1.280 g/cm<sup>3</sup>. This increase is due to the closing of lumens during the densification. One should note that after complete densification, the maximum density might reach 1.5 g/cm<sup>3</sup>. Consequently, after densification wood still possesses about 14 % porosity. The residual pores mainly remain in wood rays and also a small amount as opened lumens (Fig. 7a). Densification of wood in the radial direction not only closes the lumens but also deforms the wood rays in a 'zigzag shape' as is illustrated in Fig. 7c. This deformed shape of wood rays may influence the hydral behaviour of densified wood. It reduces the wood dilatation in the tangential direction but increases it in the radial direction.

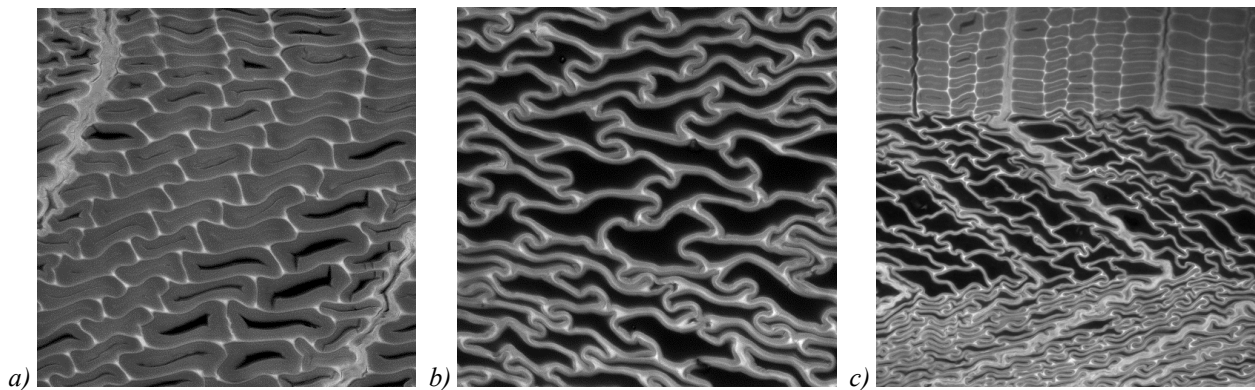
After post-treatment some observations were made on the densified specimens. Visible cracks to the naked eye were observed on the post-treated samples at the conditions of 180°C (24') and 200°C (4', 8' and 16'). These cracks were attributed to abrupt depression when blowing off. Indeed, the pressurised water kept in the sample is released by cracking it (similar to steam explosion).

Comparison of micrographs of densified wood at cellular level before and after soaking-drying tests clearly showed that the lumens of earlywood cells opened up before and more widely than the late wood cells. This was observed by confocal microscopy on typical late and early wood cells belonging to the same specimen and a typical micrograph is given in Fig. 8a-b.





**Figure 7:** a) Residual pores of latewood cells and wood rays in densified wood. b) Wood rays in non-densified simple c) Densified spruce. Densification has transformed wood rays to a zigzag form shape

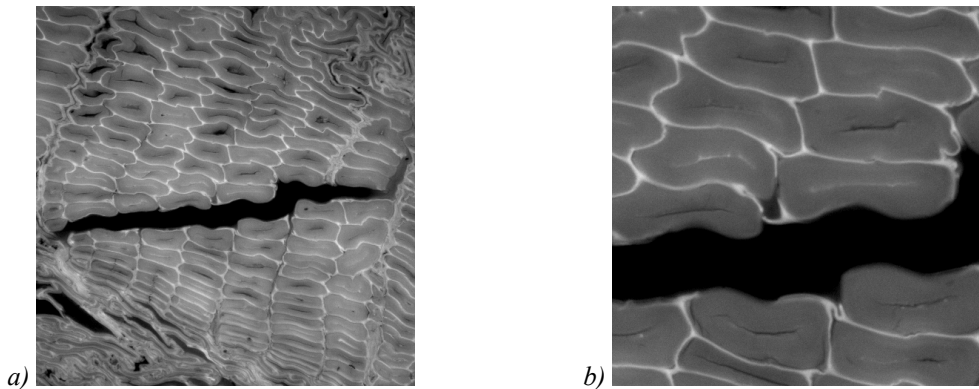


**Figure 8:** Partly recovered densified wood post-treated at 140°C and 4 hours processing time seen under confocal microscop. a) Slightly opened latewood cells. b) Widely opened earlywood cells. c) Confocal microscopic observation of latewood-earlywood cells interface after soaking-drying test

In general, earlywood cells possess bigger microfibril angles and larger lumena than latewood cells. Consequently during densification, earlywood cells undergo to bigger deformation and their microfibrils are subjected to larger internal stress than the latewood cells. During soaking-drying tests, when the physical bonds are weakened, those microfibrils with higher internal stresses go to their initial form faster. This opening seems to begin at the earlywood-latewood cells interface and progresses as the recovery increases (Fig. 8c). It is not clear when latewood cells start to open, but it takes place after the opening of the earlywood cells. Obviously it depends on the distribution of the inner stress in the cells.

The set-recovery curves given in Fig. 3 demonstrate the hydal behaviour of densified wood specimens treated by saturated steam at different temperatures and processing times. When the value of  $R_1$  of a densified specimen still tends to zero, after several soaking-drying cycles in severe conditions, one could accept that permanent fixation of compression set has been obtained. The set-recovery curves (Fig. 3) showed that complete fixation had been achieved for specimens that had undergone post-treatment at 140°C for more than 120 minutes, at 180°C for more than 15 minutes and at 200°C for more than 4 minutes. But the other samples have shown the tendency to open the closed lumens under repeating soaking-drying cycles. This can be verified by microscopic observations at the wood cell level. Besides, the set-recovery was decreased by increasing the steaming temperature or by increasing the processing time. Our primary results indicate that there might exist some type of equivalence between the effect of processing time and steaming temperature during post-treatment to obtain a wood with specified hydal behaviour. Therefore, long period post-treatment at low temperature gave to the densified

wood the same hydal behaviour as short post-treatment at high temperature. Of course this similarity does not mean that if two densified wood had shown similar hydal behaviour, they should have had similar mechanical behaviour or chemical compositions.



**Figure 9: Micrographies of 200°C, 4 min post-treated sample. a) Crack between latewood cells along middle lamella. b) Zoom of the left micrograph. Middle lamella is clearly broken by the rapid release of steam after post-treatment**

One can observe that high temperature post-treated samples get a darker colour and also become more brittle than the low temperature post-treated ones. Then the question is what are the physical mechanisms and chemical modifications, which fix permanently the compression set of densified wood treated by high temperature steaming and by low temperature steaming. Water plays two important roles in the post-treatment: on one hand it contributes to the hydrolysis of hemicelluloses and cellulose and on the other hand increases the kinetics of the reaction. So at high temperature steaming, the rate of the reaction is much higher than at low temperature steaming. One of the possible reasons for the rearrangement of the microfibrils of cellulose during post-treatment is that during high steaming temperature hemicelluloses were chemically degraded by homolytic cleavage of  $\beta$ -O-4 ether linkage (hydrolysis) in hollygosaccharides (mono-, di- and tri-saccharides). Then a part of these oligosaccharides were eluted and removed from its original inter-microfibril location by water. Consequently the cohesion between the different components of wood became weaker and so the molecular movement of microfibrils of cellulose is facilitated, especially because of the removed hemicelluloses, which leave enough room for cellulose to move. Furthermore the elution of hemicelluloses from the middle lamella might increase the wood brittleness. This phenomenon has been visualised by confocal microscopy. A typical micrograph showing a micro-crack propagated through the middle lamella is given in Fig. 9. The elution of hemicelluloses is confirmed by GPC analysis, which shows a decrease of the amount of xylose and mannose in the post-treated samples (Fig.5 b-c). Capillary viscosimetry measurements are under progress to determine the influence of the hydrolysis on the degree of polymerisation of cellulose during the post-treatment.

From a mechanical point of view, one can consider post-treated densified wood as a new brand material as its mechanical properties are highly enhanced, especially the shear resistance and the hardness. The shear resistance increases from 4.7-12.0 N/mm<sup>2</sup> to 110.6 N/mm<sup>2</sup> (Table 2) and the Brinell hardness from 12.0 N/mm<sup>2</sup> to 52.8-71.3 N/mm<sup>2</sup> (Table 3). The reason for such an increase is the closing of the lumens, which decreases the porosity from 60-75% to 10-15%. Thus, the hydal behaviour is improved. Because of the elution of hemicelluloses wood becomes less hydrophilic (Fig. 4). The number of -OH groups has been calculated with the Dent model ; it shows that half of the -OH groups are suppressed after a post-treatment at 180°C during 16 minutes. Finally, if densified wood is considered as a composite with fibres embedded in a matrix the mechanical properties of both components have to be considered to evaluate the

global mechanical behaviour.  $T_g$  of lignin has been measured by DSC in order to see if it reticulates or hydrolyses. Fig. 6 shows that lignin reticulates at the beginning of post-treatment, but is hydrolysed after long post-treatments. So an optimal duration of post-treatment with a maximum degree of reticulation could be found. On the other hand the DP of cellulose is very important too as it defines the length of the microfibrils of cellulose. With the purpose of characterising the mechanical properties of cellulose, the DP will be measured with capillary viscosimetry.

#### ACKNOWLEDGEMENT

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## Colour Modification of Wood by Light-irradiation and Heat Treatment

Katsuya Mitsui<sup>1</sup>, Akihiro Murata<sup>2</sup>, Mitsuihiro Kohara<sup>3</sup>, Satoru Tsuchikawa<sup>4</sup>

<sup>1</sup> Gifu Prefectural Human Life Technology Research Institute, Takayama 506-0058, Japan,  
mitsui@wood.rd.pref.gifu.jp

<sup>2</sup> Gifu Prefectural Human Life Technology Research Institute, Takayama 506-0058, Japan,  
murata@wood.rd.pref.gifu.jp

<sup>3</sup> Faculty of Education, Gifu University, Gifu 501-1193, Japan,  
kohara@tech.ed.gifu-u.ac.jp

<sup>4</sup> Graduate School of Bioagricultural Sciences, Nagoya University, Nagoya 464-8601, Japan,  
st3842@nuagr1.agr.nagoya-u.ac.jp

**Keywords:** Colour, Heat treatment, Light-irradiation, Relative humidity, Wavelength

### ABSTRACT

The effect of heat treatment and light-irradiation conditions on changing the colour of light-irradiated wood was investigated. Investigating the effect of heat treatment conditions, the change in the lightness ( $L^*$ ) of light-irradiated wood with heat treatment was much greater than that of unirradiated wood. The chroma coordinates ( $a^*$ ) of irradiated wood increased with treatment temperature and time. The  $b^*$  decreased after showing a sharp increase with a short period of heat treatment. It is thought that the changes are related to a change in the chemical composition which was accelerated by heat. With low temperature treatment, the colour of irradiated wood changed remarkably with high relative humidity. Little change in colour was observed with low relative humidity. Therefore, heat and the presence of water accelerated the change in the colour of irradiated wood.

The change in the colour of light-irradiated wood with heat treatment increased with light-irradiation time, and heating temperature, while the changes in the colour of wood irradiated for more than 40 to 50 hours were similar.

With the investigation of the effect of wavelength, the change in the  $L^*$  of all species tested decreased with wavelength.  $L^*$  became positive for light-irradiated Japanese cypress and hackberry; however, this effect disappeared with heat treatment. The  $a^*$  and  $b^*$  of all species were minimal when irradiated with wavelengths longer than 500 and 440 nm, respectively. However, this effect disappeared with heat treatment. In softwood,  $b^*$  was negative when exposed to light longer than 440 nm, while in hardwood, it turned negative when exposed to 390, 440, and 500 nm. However, the minimum value observed with light-irradiation disappeared with heat treatment after light-irradiation. Therefore, it is thought that chemical changes involved in the colour changes due to light-irradiation differ from those involved in the colour changes due to heat treatment.

### INTRODUCTION

The changes in colour with light-irradiation or heat treatment have been studied for many years. Generally, the wood yellows by exposure to light, and its colour difference increases with irradiation time (Tolvaj 1994, Tolvaj and Faix 1995, Park *et al.* 1996, Hon and Minemura 2001,

Ohkoshi and Saijo 2001). Hon and Minemura (2001) reported that in the photo-induced discolouration of sapwood of Japanese larch (*Larix leptolepis*), light longer than 390 nm gives rise to lightening and light shorter than 390 nm brings about darkening. Furthermore, Chang *et al.* (2000) reported that the red colour of heartwood of Japanese cedar (*Cryptomeria japonica*) is enhanced after light-irradiation of wavelengths longer than 600 nm. Park *et al.* (1996) reported that the changes in the relative ratios of absorbance at  $1730\text{ cm}^{-1}$  and  $2900\text{ cm}^{-1}$  correspond to the change in colour. However, Tolvaj and Faix (1995) claimed that the increment in new carbonyl bands in the DRIFT region between  $1650$  and  $1770\text{ cm}^{-1}$  does not signify the formation of coloured compounds with conjugated double bonds.

In colour change studies by heat treatment, the colour difference with steaming increased with increasing treatment pressure and time (Morita and Yamazumi 1987). Okuyama *et al.* (1990) reported that heating green logs increased the lightness of the black heartwood of Japanese cedar. Bourgios *et al.* (1991) reported that the decrement in lightness and the increment in the colour difference resulting from heat treatment at  $240 - 310\text{ }^{\circ}\text{C}$  are thought to result from a decrease in pentosan. Furthermore, Tolvaj *et al.* (2000) reported that steaming below  $100\text{ }^{\circ}\text{C}$  can reduce the heterogeneity of the natural colour of black locust (*Robinia pseudoacacia*) wood.

Although there are many separate reports on the change in colour by light-irradiation and by heat treatment, there are no reports on the change in colour of wood with heat treatment after light-irradiation.

This study discusses the change in wood colour resulting from heat treatment after light-irradiation.

## EXPERIMENTAL METHODS

### *Investigation of the effect of heat treatment conditions*

#### **Materials**

To investigate the effect of heat treatment conditions, the sapwood of Japanese cypress (*Chamaecyparis obtusa*) and heartwood of spruce (*Picea* sp.) were examined.

#### **Light irradiation**

Specimens were irradiated with simulated sunlight using a WEL-SUN-D (Suga Test Instruments) for 60 hours. This equipment has an irradiance of  $78.5$ ,  $176.5$  and  $311.6\text{ Wm}^{-2}$  in the region of ultraviolet ( $300 - 400\text{ nm}$ ), visible ( $400 - 700\text{ nm}$ ), and infrared ( $700 - 3000\text{ nm}$ ) light, respectively. Wavelengths below  $300\text{ nm}$  were eliminated by a glass filter. Table 1 shows the colour of specimens before and after irradiation.

*Table 1: The colour of specimens before and after irradiation*

Species	Before			After		
	L*	a*	b*	L*	a*	b*
Japanese cypress	$81.50 \pm 2.63$	$4.72 \pm 2.05$	$21.51 \pm 1.93$	$73.16 \pm 1.84$	$6.42 \pm 0.75$	$34.91 \pm 0.82$
Spruce	$76.37 \pm 2.60$	$6.30 \pm 1.26$	$20.32 \pm 1.60$	$66.20 \pm 3.41$	$8.16 \pm 1.04$	$30.11 \pm 1.71$

Note: mean  $\pm$  standard deviation

#### **Heat treatment**

After irradiation, the wood was treated under humid heat conditions at  $50$ ,  $70$ , and  $90\text{ }^{\circ}\text{C}$ ,  $90\%\text{RH}$  for up to 150 hours. Furthermore, to investigate the effect of humidity, the wood was treated at  $0$ ,  $30$ ,  $60$ , and  $90\%\text{RH}$  at a constant temperature of  $70\text{ }^{\circ}\text{C}$  for up to 150 hours. As a control, unirradiated specimens were treated at the same temperature and humidity conditions. In

addition, to make investigation into the effect of existence of oxygen in the heat treatment atmosphere, the specimens were treated with dry heat condition at 140 °C in nitrogen.

**Measurement of colour**

The colour of the surface of specimens was measured with a colourimeter (SE-2000: Nippon Denshoku Industries Co., Ltd., Tokyo). The sensor head was 10mm in diameter. Measurements were made using D<sub>65</sub> illuminant and a 2° standard observer. The tristimulus value X, Y, and Z of all specimens were obtained from the colourimeter. The CIELAB colour parameters (L\*, a\*, and b\*) were then computed, and the difference in the lightness (ΔL\*) and chroma coordinates (Δa\* and Δb\*) were calculated using the following formulae.

$$\Delta L^* = L^*_t - L^*_c$$

$$\Delta a^* = a^*_t - a^*_c$$

$$\Delta b^* = b^*_t - b^*_c$$

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

where, the subscripts *t* and *c* indicate values for the treated samples and control reference, respectively.

**Investigation of the effect of light-irradiation conditions**

**Materials**

To investigate the effect of light-irradiation conditions, sapwood of Japanese cypress, heartwood of Japanese cedar (*Cryptomeria japonica*), spruce, Japanese beech (*Fagus crenata*), Japanese oak (*Quercus crispula*), and hackberry (*Celtis occidentalis*) were examined. Table 2 shows the colour parameter of specimens.

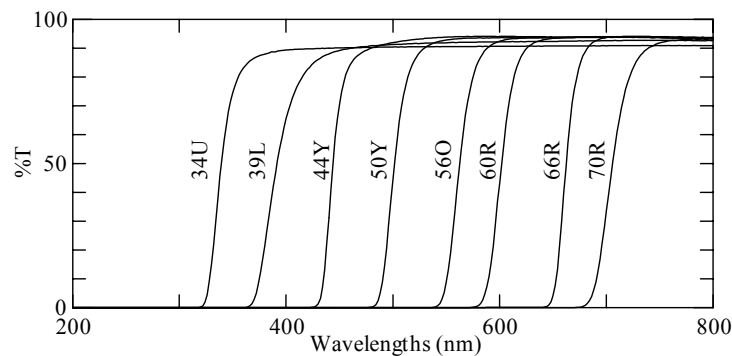
**Table 2: The colour parameter of specimens**

Species	Softwood			Species	Hardwood		
	L*	a*	b*		L*	a*	b*
Cedar	73.19±2.00	9.54±1.23	22.18±1.25	Beech	71.31±2.08	6.42±0.67	19.00±0.89
Cypress	83.52±2.50	2.93±1.79	19.80±1.53	Oak	68.14±2.03	5.91±0.58	21.17±1.20
Spruce	79.58±1.77	5.65±0.99	21.67±1.23	Hackberry	82.40±2.94	2.03±0.63	22.05±1.78

Note: mean ± standard deviation

**Light irradiation**

Specimens were irradiated with a WEL-SUN-D. To investigate the effect of light-irradiation time, the specimens were irradiated for up to 60 hours. In addition, to investigate the effect of light wavelength on discolouration, eight filters (UTF-50S-34U, SCF-50S-39L, SCF-50S-44Y, SCF-50S-50Y, SCF-50S-56O, SCF-50S-60R, SCF-50S-66R, and SCF-50S-70R: Sigma Koki Co., Ltd., Tokyo) were used to cover the surface of specimens and the specimens were irradiated for 60 hours. Fig. 1 shows the transmission curves of the various light filters.



**Figure 1: Transmission curves of filters**

## Heat treatment

After irradiation, the wood was treated under humid heat conditions at 50, 70, and 90 °C and 90%RH for up to 150 hours for investigation of effect of the irradiation time, and at 90 °C and 90%RH for investigation of effect of the wavelength.

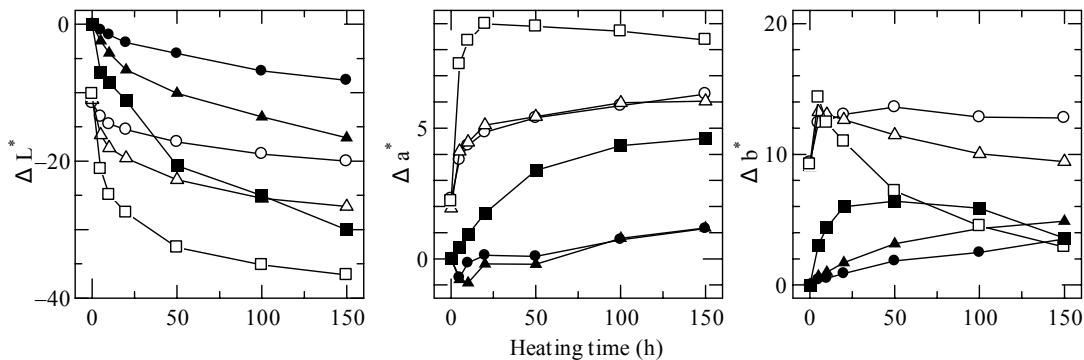
## RESULTS AND DISCUSSION

### *Effect of heat treatment conditions*

#### Dry heating in air

Fig. 2 shows the change in the colour of irradiated and unirradiated spruce with dry heating in air.  $\Delta L^*$  of both irradiated and unirradiated wood decreased with increasing temperature and treatment time.  $\Delta L^*$  of the irradiated specimen was remarkably lower than that of the unirradiated specimen. With unirradiated wood,  $\Delta a^*$  increased with treatment temperature. On the other hand, with irradiated wood,  $\Delta a^*$  increased to a constant value with temperature and treatment time and then decreased. With the unirradiated wood,  $\Delta b^*$  gradually increased with temperature and treatment time, while  $\Delta b^*$  of the irradiated wood initially increased sharply with heat treatment and then decreased. The changes in Japanese cypress were similar to those in spruce, but  $\Delta L^*$  of unirradiated Japanese cypress decreased less than that of spruce.

Colour changes in wood with light irradiation are caused by lignin and lignin derivatives (Hon and Glasser 1979). It was thought that the  $L^*$  of the irradiated wood decreased remarkably due to the impact of heat on the light-darkened lignin. Furthermore, Bourgois *et al.* (1991) reported that the decrease in  $L^*$  by heat treatment is due to the decrement in hemicellulose, especially pentosan. Therefore, it was thought that the decrement in  $L^*$  is due to not only lignin or lignin derivatives but also hemicellulose. It was thought that  $\Delta a^*$  and  $\Delta b^*$  of the irradiated specimens decreased with the decrement of  $\Delta L^*$  after the amounts of red or yellow substances initially increased with heat treatment and then became constant.



**Figure 2: Change in the colour with dry heating in air on spruce**

- : unirradiated wood heated at 120 °C, ▲: unirradiated wood heated at 140 °C,
- : unirradiated wood heated at 160 °C, ○: irradiated wood heated at 120 °C,
- : irradiated wood heated at 140 °C, ◻: irradiated wood heated at 160 °C

#### Dry heating in nitrogen

Fig. 3 shows the  $\Delta E^*$  of irradiated and unirradiated Japanese cypress heated in air and nitrogen at 140 °C for 150 hours. The  $\Delta E^*$  of irradiated wood was larger than unirradiated one. There was no significant difference between  $\Delta E^*$  of irradiated wood heated in air and in  $N_2$ , while the  $\Delta E^*$  of unirradiated wood treated in air was greater than that treated in  $N_2$ . It was thought that the change in colour was accelerated by oxidation.

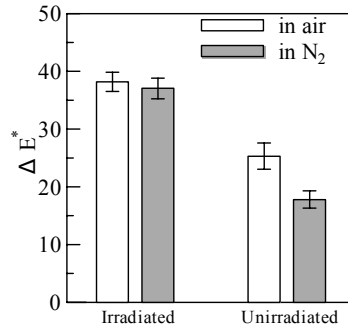


Figure 3: Effect of the presence of oxygen on colour difference of Japanese cypress

### Heating under high relative humidity

Fig. 4 shows the change in the colour of irradiated and unirradiated spruce resulting from heat treatment at a controlled humidity of 90%. The  $\Delta L^*$  of unirradiated wood barely changed with heat treatment at 50 °C. With treatment at 70 and 90 °C, it decreased with treatment time. On the other hand,  $\Delta L^*$  of the irradiated wood decreased remarkably with increasing temperature and treatment time. With unirradiated wood,  $\Delta a^*$  increased with treatment time with heat treatment at all temperatures, while with irradiated wood, it increased remarkably, became constant, and then decreased.  $\Delta b^*$  of the unirradiated wood increased with treatment time at all temperatures, while that of the irradiated wood increased remarkably at all treatment temperatures, then became constant, and ultimately decreased. In addition, the decrement was greater at higher temperatures. The changes with Japanese cypress were similar to those with spruce, although the changes in  $\Delta a^*$  and  $\Delta b^*$  were greater than those for spruce.

Goring (1963) reported that at low moisture content the softening temperature of spruce periodate lignin is about 160 °C and at higher moisture content it is lower. It was thought that the remarkable decrements in  $\Delta L^*$  of untreated wood treated 90 °C and 90% or dry unirradiated wood treated at 160 °C in air were due to the promotion of the darkening reaction by the softened lignin. Treatment at 70 °C and 90% or at 140 °C in air produced similar results. Therefore, the presence of water accelerates the change in  $\Delta L^*$  at low temperatures. The effects of treatment conditions on the changes in  $\Delta L^*$  of the irradiated wood correspond to those in loss of strength or weight reported by Stamm (1956).

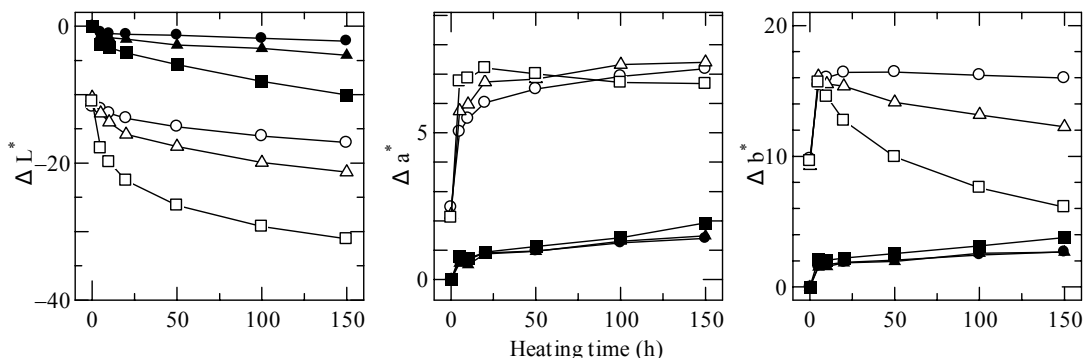


Figure 4: Change in the colour with heat treatment under high relative humidity on spruce

- : unirradiated wood heated at 50 °C 90%RH, ▲: unirradiated wood heated at 70 °C 90%RH,
- : unirradiated wood heated at 90 °C 90%RH, ○: irradiated wood heated at 50 °C 90%RH,
- : irradiated wood heated at 70 °C 90%RH, □: irradiated wood heated at 90 °C 90%RH



### Relative humidity in treatment atmosphere

Fig. 5 shows the effect of relative humidity on irradiated and unirradiated Japanese cypress. The  $\Delta L^*$  of unirradiated wood hardly changed, while that of the irradiated one decreased with high relative humidity and treatment time. In spruce,  $\Delta L^*$  of both unirradiated and irradiated wood decreased with high relative humidity and treatment time. The decrement was greater in irradiated wood than in unirradiated wood.  $\Delta a^*$  of irradiated wood increased with relative humidity and treatment, while that of unirradiated wood hardly changed.  $\Delta L^*$  and  $\Delta b^*$  remarkably changed when the relative humidity exceeded 60%. Therefore, treatment at a relative humidity exceeding 60% affected the change in wood colour.

Kondo *et al.* (1986) reported that oxygen concentration and relative humidity influenced the colour change of moulmein rosewood (*Millettia* sp.). Stamm (1956) reported that the degree of thermal degradation differed with the presence or absence of air. In the presence of air, the degradation of wood is greater than with heat treatment in an inert gas, due to oxidation. Therefore, the decrement of  $L^*$  and the remarkable change in  $a^*$  and  $b^*$  were not only promoted by heat treatment and the presence of humidity, but also by the presence of oxygen. The factors affecting the change in wood colour with heat treatment are lignin and hemicellulose, although the effect of its derivatives must be examined in detail because the degree of change differs among species.

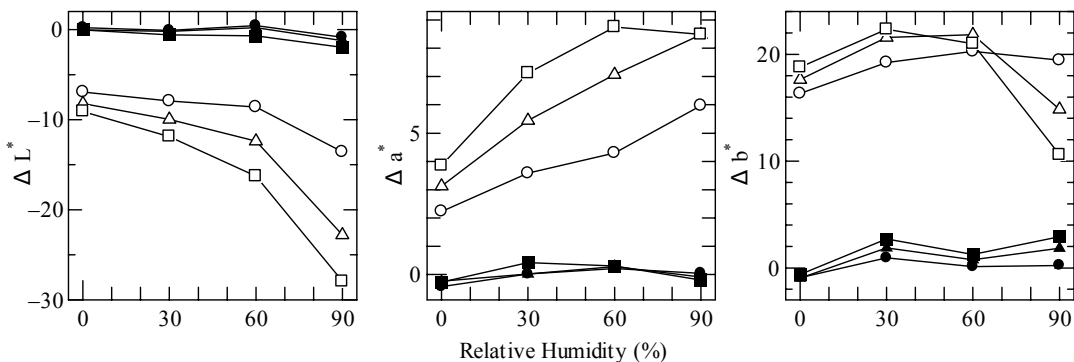


Figure 5: Effect of relative humidity to change in the colour on Japanese cypress

- : unirradiated wood heated at 70 °C for 5 hours, ▲: unirradiated wood heated at 70 °C for 50 hours,
- : unirradiated wood heated at 70 °C for 150 hours, ○: irradiated wood heated at 70 °C for 5 hours,
- ◻: irradiated wood heated at 70 for 50 hours, ◻: irradiated wood heated at 90 °C for 150 hours

### Effect of light irradiation conditions

#### Irradiation time

Fig. 6 shows the changes in  $\Delta L^*$ ,  $\Delta a^*$ , and  $\Delta b^*$  with heat treatment for Japanese cypress.  $\Delta L^*$  decreased with length of light-irradiation and heat treatment for all species.  $\Delta a^*$  increased with heat treatment for short irradiation times, reached a constant value with irradiation time and heat treatment temperature, and then decreased. The constant values for Japanese cedar, Japanese cypress, spruce, Japanese beech, Japanese oak, and hackberry were  $\Delta a^* = 3 - 5, 10, 7 - 8, 5, 5,$  and  $11 - 12,$  respectively. Although heating temperature produced obvious differences in Japanese cedar, Japanese cypress, spruce, and hackberry, there was little difference in Japanese beech and Japanese oak. When the irradiation time exceeded 40 - 50 hours, the change in colour with heat treatment was almost equivalent in all species.  $\Delta b^*$  of the irradiated wood initially increased sharply with heat treatment, and then reached a constant value. With a long irradiation time and high heat treatment temperature,  $\Delta b^*$  decreased remarkably, while with a short

irradiation time or low heat treatment temperature, it remained constant or gradually decreased. The changes in  $\Delta b^*$  and  $\Delta a^*$  behaved similarly when the irradiation time exceeded 30–40 hours. When the irradiation time is short, a small amount of energy is transferred to the wood. Therefore, it is believed that the wood does not photolyse sufficiently, and the change in colour with heat treatment after light-irradiation is small.

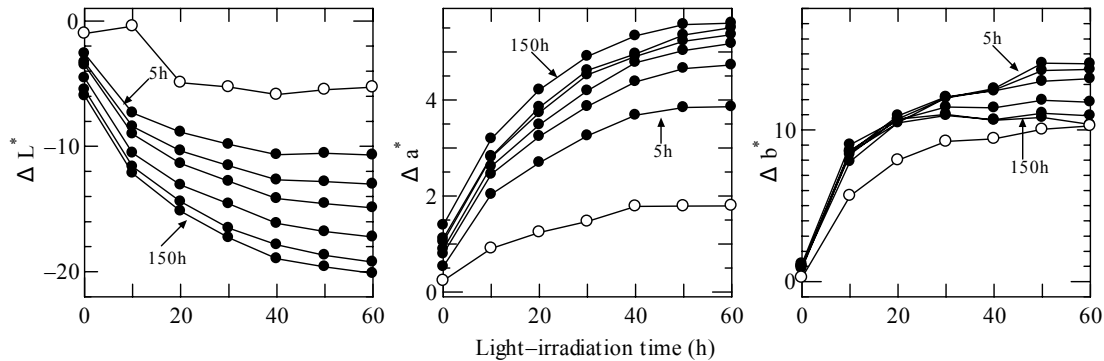


Figure 6: Effect of light-irradiation time to change in the colour on Japanese beech

○: light-irradiation, ●: heat treatment

### Wavelength

Fig. 7 shows the changes in the colour of Japanese cypress with heat treatment after light-irradiation using various light filters.  $\Delta L^*$  decreased with treatment time. The degree of change was greater in the specimens irradiated with light at shorter wavelengths. The behaviour of specimens irradiated using filters that eliminated wavelengths shorter than 600 nm was similar to that of specimens covered with aluminium foil when exposed to light, *i.e.*, control specimens that were heated without exposure to light. The changes in all species were similar to those in Japanese cypress.

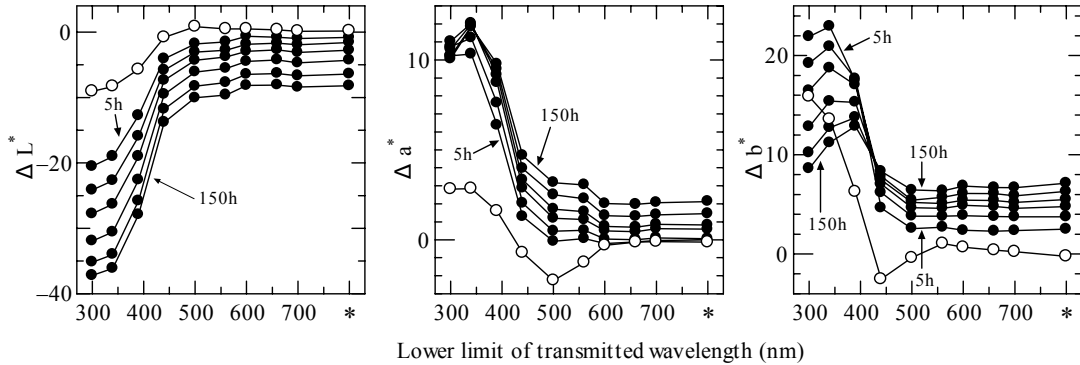
$\Delta a^*$  increased with treatment time, and the increase was most pronounced at 300 and 340 nm. The specimens irradiated with light longer than 600 nm behaved in a manner similar to control specimens covered with aluminium foil. Like the changes in  $\Delta L^*$ , the changes in  $\Delta a^*$  in all species were similar to those in Japanese cypress.

The  $\Delta b^*$  of specimens exposed to light at 300, 340, and 390 nm increased remarkably with a short exposure, and then decreased with increasing treatment time. The  $\Delta b^*$  of specimens irradiated at wavelengths longer than 440 nm increased with treatment time. In all species, the changes in  $\Delta b^*$  with light longer than 500 nm were similar to those of heat-treated control specimens.

The  $\Delta L^*$  of Japanese cypress and hackberry was maximal when exposed to wavelengths longer than 500 nm, while the  $\Delta a^*$  and  $\Delta b^*$  of all species became minimal with wavelengths longer than 500 and 440 nm, respectively. These phenomena were not observed when specimens were heat-treated after light-irradiation. It is thought that the chemical changes related to changes in colour with light-irradiation were not the same as those involved in changes in colour with heat treatment after light-irradiation.

In this study, we examined with an artificial sunlight, which has spectral distribution. Therefore, these phenomena are not necessarily observed by light-irradiation with another light source. Recently, to eliminate spectral distribution, some researches of photodegradation by laser have been carried out (Barta *et al.* 1998, Barta *et al.* 1999, Košíková *et al.* 2001). The laser has several

advantages compared to traditional UV-sources. By utilising laser light, the time of interaction can be shortened, the degradation caused by UV-light can be studied, excluding the thermal effects originating from temperature rise of the surface. Furthermore, the wavelength of irradiation, an amount of energy, and the intensity of irradiation can be determined. We have to consider also the application of laser instead of traditional light source.



**Figure 7: Changes in the colour of Japanese cypress with heat treatment after light-irradiation with various filters**

○: light-irradiation for 60 hours, ●: heat treatment, \*: specimens covered with aluminium foil

Generally, wood is coloured by painting. Wood painting has mainly two objectives. One is colouring, the other is the protection of the surface. However, the emission of volatile organic compounds such as toluene and xylene from paint is a health concern. Colouring by light-irradiation and heat treatment emits no volatile organic compounds and is very simple. Furthermore, there is less damage, such as cracking and bending, because the wood is treated at a comparatively low temperature. This treatment method can make various brownish colours with controlling heating temperature, heating time, relative humidity, light-irradiation time, and wavelength. Therefore, this treatment is a new colouring method. In addition, photographs or illustrations can be printed on the surface of wood when the surfaces are covered with films before wood is exposed to light. However, it must be treated or coated in some way to protect the surfaces of wood. In a future study, we will discuss the changes in the chemical components, shortening of treatment time, and application to industrial size.

## CONCLUSIONS

We discussed the changes in the colour of light-irradiated wood resulting from heat treatment. The changes in  $\Delta L^*$  of irradiated wood as a result of both dry heating and heating at a high relative humidity were greater than those in unirradiated wood. Also,  $\Delta a^*$  and  $\Delta b^*$  of irradiated wood changed remarkably in comparison with unirradiated wood. These changes were barely observed when heating occurred at a low relative humidity. Therefore, not only heat, but also the presence of water and oxygen, promoted changes in the colour of light-irradiated wood. The change in colour of light-irradiated wood with heat treatment increased with light-irradiation time, heating time, and heating temperature, while the changes in the colour of wood irradiated for more than 40 to 50 hours were similar. It is thought that the light between 440 and 600 nm has bleaching effect to wood. The maximum value of  $\Delta L^*$  and the minimum values of  $\Delta a^*$  and  $\Delta b^*$  produced by light-irradiation disappeared with heat treatment after light-irradiation.

## ACKNOWLEDGEMENT

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**OIL AND HEAT TREATMENTS**  
POSTER PRESENTATIONS



## Characterisation of Gaseous Emissions from a Small-Size Industrial Plant for Thermal Wood Modification by GC/MS

Niv Graf, Wilhelm Haas, Herbert Böchzelt

Joanneum Research, Institute for Sustainable Techniques and Systems, Elisabethstrasse 16/I,  
8010 Graz, Austria

**Keywords:** wood, heat treatment, emission, analyses, GC/MS

### ABSTRACT

Environmentally sound wood protection and preservation methods have become increasingly important due to public and legal demand. Chemical, biological or thermal treatment of wood is a convenient method to achieve this goal. Nowadays, thermal modification of wood has become a well established procedure, and there are a growing number of industrial treatment centres all around Europe. So far, the work has been mainly focused on developing and improving different treatment processes and characterisation of the thermally modified wood products. Yet there is little information available about the condensable gaseous emissions from the treatment processes. In general, all gaseous emissions are burnt to fulfill environmental regulations, although preliminary scientific work indicates that some of the emitted compounds could be utilised in various ways and therefore should be considered as valuable by-products. Our work aims at the characterisation of these gaseous emissions. The study is conducted in cooperation with a thermal wood treatment plant in Austria. Condensates of the gaseous emissions are characterized by GC/MS. Within this report, investigations on heat treated European spruce (*Picea abies*) are presented.

### INTRODUCTION

Environmentally sound wood protection and preservation methods have become increasingly important due to public and legal demand. Thermal treatment of wood has lately grown in interest as a modification method for several reasons: there are already well established processes, no chemicals are applied during the treatment, a positive influence on different wood properties (e.g. reduced swelling and shrinking, better resistance against fungal attack/decay, colour change of treated wood welcome as an important style element, easy to handle at end of lifetime, etc.) (Militz 2002). The key to all thermal treatment processes is to keep the wood treated at an elevated temperature in a range of about 180-220 °C. Other important process parameters are: pretreatment, duration of high-temperature interval, atmosphere within the reactor, post treatment. All these have a significant influence on the chemical reactions within wood. Generally speaking, a more or less significant mass loss takes place depending on the treatment temperature (Hanger *et al.* 2002). This is due to complex chemical reactions and partial degradation of some wood constituents, mainly hemicelluloses. Cellulose and lignins are more resistant to thermochemical degradation. Many of the reaction mechanism and the changes in the chemical composition of heat treated wood are already well investigated (Viitaniemi *et al.*, 2001). However, there is only limited data available on the volatile organic compounds, which are released during the heat treatment of wood.

Our work aims at the characterisation of these emissions, and is focused on the condensable gases emitted by a wood treatment plant. It is intended to determine if the emissions contain



compounds considered to be valuable products and if they could be obtained in amounts, which are sufficient for an economically viable recovery.

## EXPERIMENTAL METHODS

### *Materials and sampling method*

The wood material treated in the monitored industrial process was air-dried (moisture content around 20%) and bark free European spruce (*Picea abies*). The treatment was carried out in a small-size Austrian plant, equipped with a heating chamber with a maximum capacity of 15 m<sup>3</sup> of wood per treatment. Together with the regular load of wood, 8 small wooden boards (400 x 200 x 10mm) were treated to determine mass loss. During the whole process, the pressure and the temperature in the chamber as well as wood temperature were monitored. Emission samples were taken directly from the chambers' flue-gas line by means of a small testing tube (12 mm I.D.). Compounds were collected through condensation in a condenser followed by a gas-trap. A weak vacuum was maintained in the gas collecting unit to ensure constant gas flow. After each sample collection, the condenser and the gas trap were carefully washed with acetone. The washing solutions were collected for successive analyses.

### *Analytical methods*

The volatile organic compounds in the liquid, aqueous phase collected from condensation were extracted with dichloromethane (CH<sub>2</sub>Cl<sub>2</sub>), while acetone samples from washing were used without further treatment. Analyses of both were carried out by GC/MS. A J&W DB-5MS (122-5562) capillary column (15 m x 0.25 mm; film thickness 0.25 µm) was used. Helium was used as a carrier gas with a flow rate of 1 mL min<sup>-1</sup>. The split-ratio was 20:1. The temperature program was as follows: start at 40 °C, 10 °C min<sup>-1</sup> to 300 °C, 10 min at 300 °C. Injection volume was 1 µL, injection port temperature was set at 220 °C, detector temperature was at 280 °C. For interpretations, the obtained mass spectra were matched with data from a comprehensive electronic database. The TOC and the pH – values of the samples were also determined. Average mass loss was measured by drying (105 °C, 24 h) and weighing 8 small wooden boards before and after heat treatment.

## RESULTS AND DISCUSSION

Table 1 shows TOC and pH-values of the examined liquid samples as well as the average wood temperature at time of sampling during the monitored treatment process. Time refers to the approximate duration of the treatment process at the moment of sampling. Sampling time was 30 minutes.

*Table 1: TOC- and pH – values of tested samples in regard to wood temperature and duration of treatment*

Sample no.	PH	TOC [mgL <sup>-1</sup> ]	Temperature [°C]	Time [h]
1	2.7	2690	115 - 117	21
2	2.7	3120	137 - 143	25.5
3	2.6	5820	153 - 158	27
4	2.5	10650	167 - 171	28.5
5	2.5	22750	182	30
6	2.5	20990	182	31.5
7	2.4	26100	176	33

The pH-values may indicate increasing levels of organic acids emitted over the period of the treatment. TOC values increase, corresponding to increasing temperature and remain almost constant at the temperature plateau (180 °C), which shows the strong influence of temperature on degradation and emission of VOCs in wood. Mass loss of treated spruce was determined at 2,6% of initial dry substance (DS). This is in good agreement with comparable data from the literature (Alén *et al.* 2002). The identified main components from the GC/MS analyses in the condensed gas samples are: acetic acid, furfural, dimethylglyoxal, hydroxyacetone, toluene and various terpenes (mainly  $\alpha$ -pinene). Levels of acetic acid and hydroxy-ketones continually rise from sample 4 to 7. As for the acetone phase the identified main components are: various terpenes (mainly  $\alpha$ -pinene, but also limonene,  $\beta$ -pinene and  $\delta$ -carene), 4-hydroxy-4-methyl-pentanone, acetic acid and furfural. Significant levels of various terpenes emitted throughout the process (mainly found in the acetone phase) indicate that their emission takes place continuously over the whole process. The identified main components have a wide field of application in the chemical and pharmaceutical industries already, therefore they should be considered as highly valuable by-products.

## CONCLUSIONS

The aim of this study was to get information on the emissions of an industrial-plant heat treatment process [treatment of European spruce (*Picea abies*)]. A first qualitative study of the emitted components was carried out successfully. The data offers information on the composition of the emissions during the whole process. The identified compounds are considered as interesting products for various industrial uses.

## ACKNOWLEDGEMENTS

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## Evolution of Wood Hydrophobic Properties During Heat Treatment

Mohammed Hakkou<sup>1</sup>, Mathieu Pétrissans<sup>1</sup>, Idriss El Bakali<sup>2</sup>, Philippe Gérardin<sup>1</sup>, André Zoulalian<sup>1</sup>

<sup>1</sup>LERMAB UMR 1093 INRA/ENGREF/UHP, Université Henri Poincaré, BP 239, 54506 Vandoeuvre les Nancy, France. Mathieu.Petrissans@lermab.uhp-nancy.fr

<sup>2</sup>Laboratoire de Chimie Physique, Université Sidi Mohamed Ben Abdellah, Faculté des Sciences Dhar Mehraz, Fes, Maroc

**Keywords:** hydrophobicity, wettability, contact angle, heat-treated wood, chemical modification

### ABSTRACT

The aim of this work was to study wettability variations during heat treatment of wood. The heat treatment has been carried out in the temperature range of 40 to 260°C under an inert atmosphere on four European wood species (pine, spruce, beech and poplar). The contact angle values, measured by the Wilhelmy technique, after the heat treatment indicated a significant increase of the wood hydrophobicity at around 135°C. Mass loss measurements indicate that chemical modifications and formation of volatile compounds through degradation reactions are not the origin of this change. Similarly, generation of extractives, during the heat treatment, do not explain the wettability evolution. These results suggest that wettability modification during heat treatment is due to other factors involving low chemical modification of wood components.

### INTRODUCTION

A new product called torrefied or retified wood can be obtained by mild pyrolysis of wood in the temperature range of 200 to 260°C under an inert atmosphere. After torrefaction, the wood possesses some new properties: reduced hygroscopicity, improved dimensional stability and durability (Tjeerdsma *et al.* 1998). The principal disadvantage of the torrefied wood is its increased rigidity. Another parameter often mentioned but not well investigated is the hydrophobic character. Wood, which is naturally hydrophilic, becomes after heat treatment hydrophobic which could generate important problems during varnish or paint deposition. The aim of our study is to characterise the wettability evolution during heat treatment and to try to explain this evolution through mass loss or extractives generation.

Wood wettability is generally difficult to measure. The heterogeneous and porous character of this material involves an important hysteresis (Liptáková and Kúdela 1994). Moreover, the wood extractives may also contaminate the probe liquids during the measurement (Wålinder and Johansson 2001). All these problems make wood wettability difficult to measure. The notion of wettability is based on the concept of an equilibrium state (Young 1805), between the interfacial surface tension of the three phases (liquid, solid, vapor) leading to the existence of an equilibrium contact angle. This contact angle is determined by the equation (1) known in the literature as the Young's relation.

$$\gamma_{SV} = \gamma_{SL} + \gamma_{LV} \cos \theta \quad (1)$$

Where  $\gamma$  is the interfacial surface tension (for solid-vapor (SV), solid-liquid (SL), and liquid-vapor (LV)) and  $\theta$  is the equilibrium contact angle. Contact angle of a droplet deposited on a real solid surface can take several values. The difference between the higher and the lower values of this dispersion is called hysteresis of the contact angle. This last characteristic is related to the chemical heterogeneity (Menawat *et al.* 1984) and to the solid roughness (Dettre and Johnson 1964). The lower contact angle is called receding contact angle ( $\theta_r$ ) and the higher is called advancing contact angle ( $\theta_a$ ). The Wilhelmy method chosen for this study (Wålinder and Johansson 2001, Wålinder and Ström 2001) is a not conventional technique for wood contact angle measurement but seems to give good results on this material. In addition to the  $\theta$  measurement, we have investigated mass loss of wood sample and the extractives generation during the heat treatment.

## EXPERIMENTAL METHODS

### *Contact angle measurement*

Immersing a sample plate of wood into a probe liquid (water) allows the determination of advancing and receding contact angles using the Wilhelmy method. The force on the plate and the immersion depth have been measured during the test cycle. The Wilhelmy force  $F_w$  has an effect on the liquid surface only. During the immersion cycle this force remains constant and obeys to the equation (2) :

$$F_w = \cos\theta \gamma P \quad (2)$$

Where  $\gamma$  is the liquid surface tension and  $P$  is the wetted circumvented length or perimeter. The lifting force  $F_a$  (buoyancy force), is given by the equation (3)

$$F_a = \rho g l w h \quad (3)$$

Where  $\rho$  is the density of liquid,  $g$  is the gravitation constant,  $l$  and  $w$  are respectively the length and the thickness of the plate.

The linear function, which describes the resulting force  $F$  ( $F = F_w - F_a$ ) measured by the tensiometer, can be calculated from a regression line. The corresponding contact angle has been calculated from the equation (4).

$$\cos\theta = \frac{(F + F_a)}{\gamma P} \quad (4)$$

The measuring unit (Tensiometer K12, Krüss GmbH, Hambourg, Germany) consisted of a force measuring system and a platform drive system. The measuring precision of the tensiometer is  $0.02 \text{ mN.m}^{-1}$ . The immersion velocity was fixed at  $6 \text{ mm min}^{-1}$ . The wood sample was immersed along the radial direction, to a depth of 5 mm. All the measurements were performed in the conditions of a room temperature  $20 \text{ }^\circ\text{C}$  and a relative humidity of order of 40-50 %.

### *Wood samples for contact angle measurement*

Four wood species have been studied : *Picea karst* (spruce), *Populus nigra* (poplar), *Fagus sylvatica* (beech), and *Pinus sylvestris* (pine). The wood plate was of the following dimensions : length 20 mm (radial direction), thickness 1 mm (longitudinal direction), and height 10 mm (tangential direction).

**Heat-Treatment**

The heat-treatment of wood was performed in a reactor placed in an oven for 10 temperature steps between 40 and 260°C, for 8 hours. The oven temperature was increased by 20°C min<sup>-1</sup> from ambient to the desired operating temperature.

**Mass loss of wood samples**

Mass loss after heat treatment was estimated according to equation 5:

$$ML(\%) = \frac{m_{ht} - m_i}{m_i} \times 100 \quad (5)$$

Where  $m_i$  is the oven dried (80°C) mass of the sample before treatment and  $m_{ht}$  the oven dried mass of the same sample after heat treatment.

**Extractives generation**

Extractives generation was recorded only on the experiment performed with the beech samples. For this purpose we used two consecutive extractions with an ASE 200 Dionex extractor (100bar, 15mn) using initially hexane and subsequently a toluene/ethanol mixture (2/1, v/v). Extractives generation was estimated after solvent evaporation, by sample weighing.

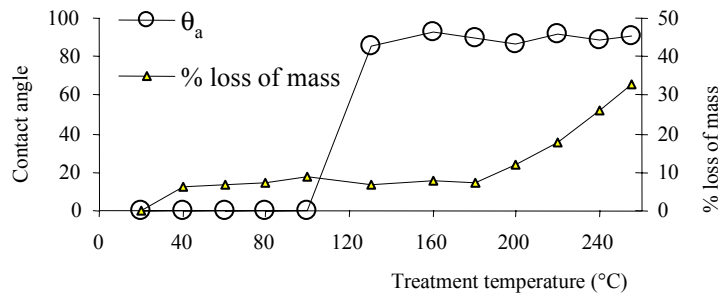
**RESULTS AND DISCUSSION**

The advancing contact angle and the mass loss are presented for the different wood species in Fig. 1, 2, 3 and 4. As it is often reported in the literature the receding contact angle  $\theta_r$  of a water droplet deposited on wood is equal to zero (Deng and Abazeri 1998, Wälinder and Ström 2001). These observations are confirmed by the present study, i.e. no receding contact angles can be obtained on the wood samples. Advancing contact angle values increase from 0 to 90° for a temperature treatment around 135°C. At this relatively low temperature, wood naturally hydrophilic, becomes hydrophobic. This radical change is observed for the four wood species. In order to better understand this result we have compared contact angle evolution and the mass loss.

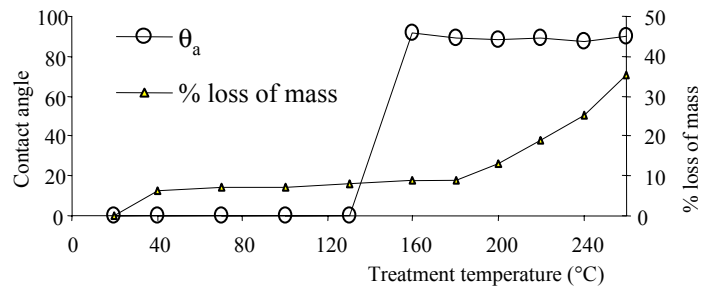
The mass evolution starts with a loss of 7%. This stage corresponds to the wood drying phase. In the temperature range of 80 to 200°C the wood mass does not vary. When the temperature becomes greater than 200°C, the mass loss is important. At 260°C, the wood sample loses 30 to 35% of its initial mass. Mass loss can be explained by hemicellulose degradation (Weiland *et al.* 1998, Weiland and Guyonnet 2001, Alén *et al.* 2002). As shown in Figs. 1, 2, 3, and 4, there is no direct relation between the contact angle evolution and the mass change.

Fig. 5 shows extractives generation during beech heat treatment. The first part of the curve corresponds to the presence of native extractives of about 1% (beech). Generation of extractives was effective at 160°C. This production was probably due to a beginning of hemicellulose decomposition. As for mass loss, extractives generation during heat treatment does not explain wettability evolution.

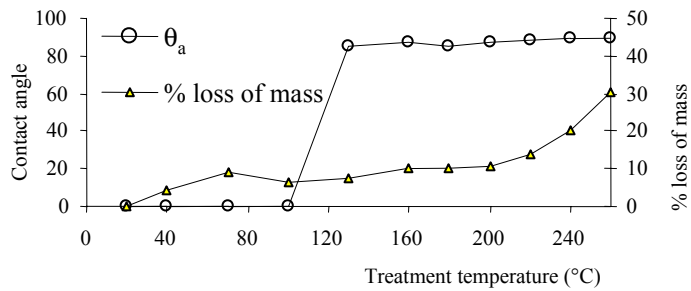
These observations suggest that wettability evolution is not correlated with an important chemical modification nor degradation of wood. Only chemical reactions, without important mass loss or extractive generation, are responsible for the hydrophobic character. Among these reactions, it is possible that thermoreticulation reactions (Tjeerdsma *et al.* 1998) involving dehydration or deacetylation reactions lead to a new composite between wood's components with improved water repellency properties.



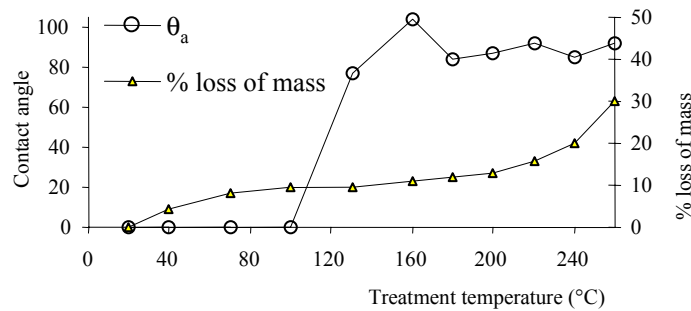
**Fig. 1: Contact angle and mass loss evolution during poplar heat treatment**



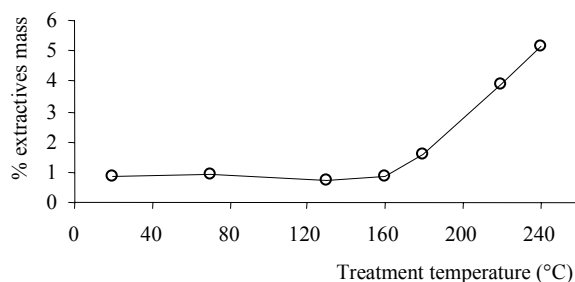
**Fig. 2: Contact angle and mass loss evolution during beech heat treatment**



**Fig. 3: Contact angle and mass loss evolution during spruce heat treatment**



**Fig. 4: Contact angle and mass loss evolution during pine heat treatment**



**Fig. 5: Extractives generation (%) during beech heat treatment**

## CONCLUSIONS

Wood, naturally hydrophilic, becomes hydrophobic after heat treatment at about 135°C. This radical evolution is reproducible for the four European wood species studied and can't be explained by an important thermal degradation of the main wood constituents. In the same way, generation of extractives is not responsible for the wetting change. This change has significant consequences, in particular for the deposit of paint.

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## Surface Analyses of Chemically and Thermally Modified Wood by FT-NIR

Barbara Hinterstoisser<sup>1,3</sup>, Manfred Schwanninger<sup>1,3</sup>, Barbara Stefke<sup>1,3</sup>,  
Robert Stingl<sup>2</sup> and Margareta Patzelt<sup>2</sup>

<sup>1</sup> Institute of Chemistry, BOKU – University of Natural Resources and Applied Life Sciences, Vienna;  
Muthgasse 18, A-1190 Vienna, AUSTRIA, Email: bhinter@edv2.boku.ac.at

<sup>2</sup> Institute of Wood Science and Technology, BOKU – University of Natural Resources and Applied Life  
Sciences, Vienna; Gregor Mendel Str. 33, A-1180 Vienna, Austria

<sup>3</sup> Competence Centre for Wood Composites and Wood Chemistry (WOOD *K plus*), Muthgasse 18, A-  
1190 Wien, Austria

**Keywords:** FT-NIR spectroscopy, thermal wood modification, acetylation, surface analysis

### ABSTRACT

Wood modification, as a high priority topic of wood researchers and industry, needs an easy to use, fast and cheap analytical technique, to monitor the modification process. Near Infrared (NIR) spectroscopy is a very promising technique for this purpose. Spruce wood (*Picea abies* (L.) Karst.) modified by thermal treatment and chemically by acetylation was investigated by NIR spectroscopy using a fibre optic probe. This technique was chosen as it is an easy to handle technique with hardly any need of sophisticated sample preparation and very low running costs. Furthermore, although the spectra are quite unstructured, as they consist of highly overlapping bands, they have a high information content. NIR spectra can be used for drawing qualitative as well as quantitative conclusions about the chemical changes. Spectra were recorded by means of a fibre optic probe dipping into wood meal taken from the surface of modified and unmodified samples. Changes over the time of treatment could be followed easily. In several processes, the knowledge of the identity or the affiliation to a group or class already fulfils the requirements. This means that no reference values are needed and therefore only spectra of reference samples will be necessary for classification. For example, the separation of thermally modified wood samples into clusters according to their treatment (0 to 48 hours) is shown, affirming the feasibility of FT-NIR – spectroscopy for quality control. Despite all these advantages it has to be stated, that FT-NIR spectroscopy is a “secondary method” and therefore reference values are still needed for calibration.

### INTRODUCTION

The change of wood properties through chemical and thermal modification techniques has an already long tradition and became a research topic again in the last decades for scientists as well as for industry. By that the need for suitable, cheap, easy to apply and fast analytical techniques, to control the modification processes became an important topic. FT-NIR spectroscopy, using the near infrared light, has received the interest of wood scientists during the last decade. As NIR-spectra present highly overlapping bands (overtone and combination vibrations, mainly of OH, NH and CH functionalities) it is hardly possible to assign single bands. Therefore, second derivative spectra, as well as multivariate data analysis is mostly used to interpret the spectra (Faix 1992, Meder *et al.* 1994, Olsson *et al.* 1995). NIR has been used *e.g.* to determine the content of wood components like lignin, cellulose and extractives, to estimate fibre orientation,

moisture content, kappa number, pulp yield and mechanical properties of wood (e.g. Michell 1995, Gindl *et al.* 2002, Gierlinger *et al.* 2002). FT-NIR spectroscopy provides the possibility to easily obtain information on effects of different modification processes like thermal or chemical treatment (Schwanninger *et al.* 2002, Hinterstoisser *et al.* 2002). Thermal modification causes a partial decomposition of wooden components followed, for instance, by a change of surface properties (Patzelt *et al.* 2002). Acetylation is among the most intensively described methods of chemical modification of wooden materials. It dramatically changes the surface properties, as the hydrophilic OH-groups are changed against O-acetyl groups (Stefke *et al.* 2002). In the presented paper it is shown that *via* FT-NIR, it is possible to follow chemical changes occurring on the surface in consequence of acetylation and thermal treatment. Furthermore, it is shown to be useful for distinguishing different treatment levels of the processes.

## EXPERIMENTAL

For thermal treatment, samples of spruce wood (*Picea abies* (L.) Karst.) with a moisture content of about 19% were put in a reactor. The reactor was evacuated, filled with nitrogen and a pressure of 0.8 MPa was applied. Subsequently, the temperature was raised to 440 K. The samples were treated at this temperature for 0 hours (reference), 1.5 h, 3 h, 6 h, 9 h, 18 h and 48h.

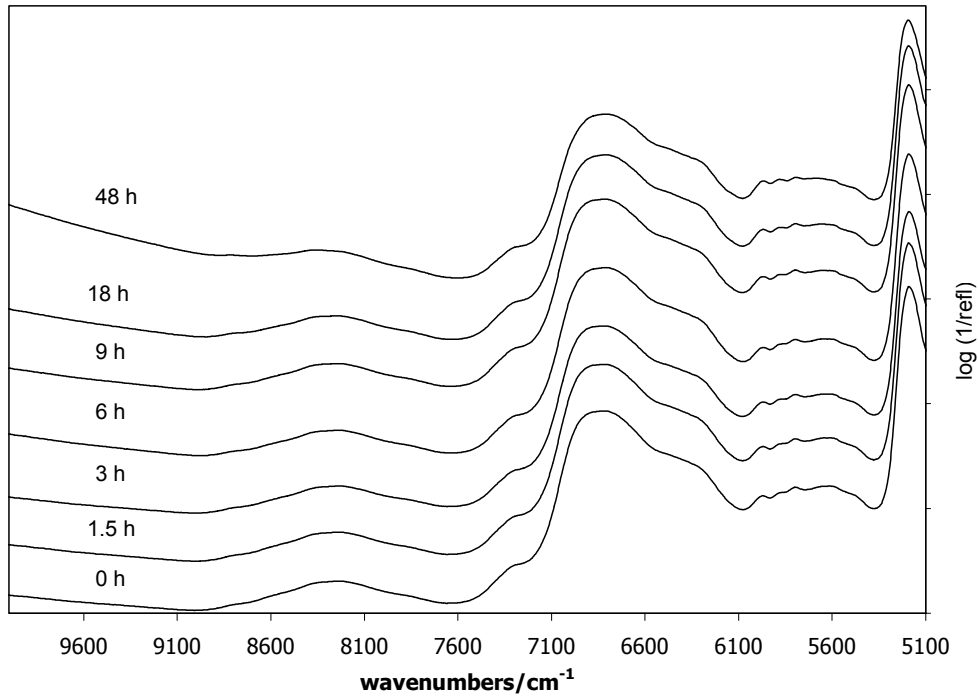
The chemical modification was done using dried spruce wood veneers. These were treated in different reaction systems (pure acetic anhydride, acetic anhydride with 0.5%, 1.0%, 5.0% and 10% v/v pyridine, "liquid phase acetylation") for varying times (15 to 270 minutes). The procedure was followed by extraction with acetone and drying at 105 °C.

The FT-NIR spectra of the samples (ground wood of the surface) were recorded using BRUKER Equinox 55 spectrometer, equipped with a Ge-diode detector and a fibre optic probe. The recorded NIR region was 10 000 to 5100  $\text{cm}^{-1}$ . The spectra were measured in reflection mode. 100 scans per sample were collected at a spectral resolution of 10  $\text{cm}^{-1}$  and averaged. The average spectra were chosen for further calculations. The reflection was transferred to absorption units (log 1/reflexion). Spectralon, a thermoplastic resin, served as reference.

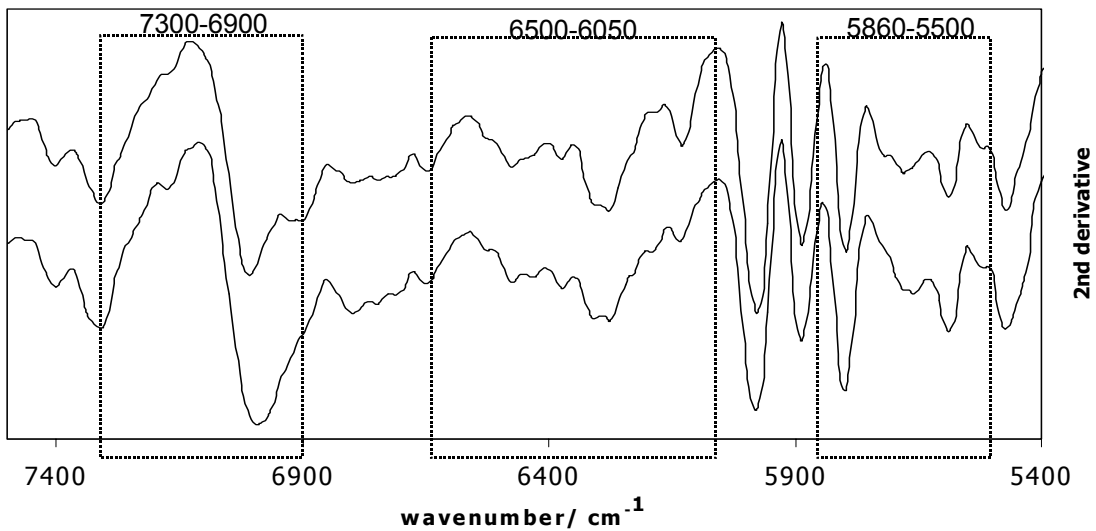
## RESULTS AND DISCUSSION

### *Thermally modified wood*

Figure 1 presents NIR spectra of thermally modified spruce wood, treated for 0 up to 48 hours. Only minor differences can be discerned, comparing the spectra. To eliminate differences deriving from baseline shifts and scattering effects, second derivative spectra were calculated. The obtained spectra are shown in figure 2. This spectral data set was used to perform cluster analysis. A classification of the thermal modified wood, according to the different treatments was possible (Fig. 3). The derivative spectra had to be normalised and were ordered into hierarchical clusters using Ward's technique (Otto 1997). The spectral data of the wavenumber regions 7300-6900  $\text{cm}^{-1}$ , 6600-6050  $\text{cm}^{-1}$  and 5860-5500  $\text{cm}^{-1}$  were used for these calculations.



*Figure 1: NIR-spectra of thermally modified spruce wood (between 0 and 48 hours treatment)*



*Figure 2: Second derivative spectra of untreated (lower spectrum) and 48h thermally modified wood (upper one). The marked wavenumbers ranges were used for cluster analysis.*

A small difference in heterogeneity in figure 3 represents high similarity of the spectra and therefore, of the samples. As expected, the difference between the sample charge A, treated for 48 hours and the sample charge F, treated for 18 hours is very obvious. Smaller differences are observed for samples treated between 3-9 hours. The presented results give very good evidence that in general, a classification of the samples according to the length of treatment is possible. An easy to apply tool is provided by that.

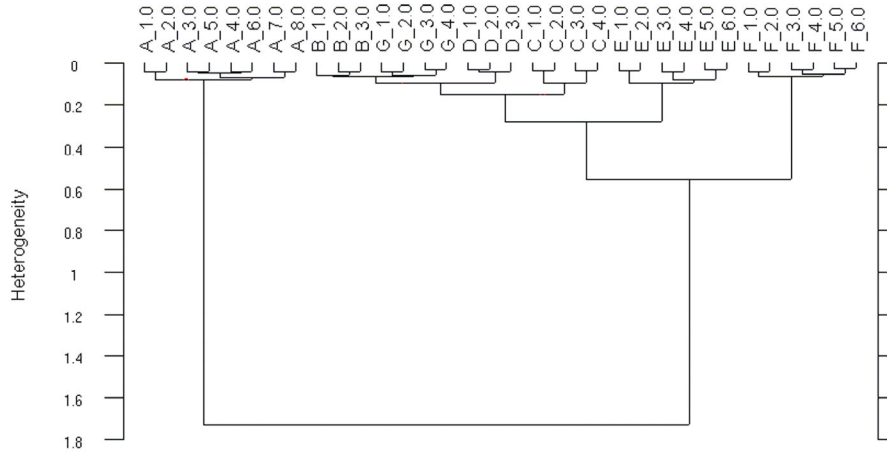


Figure 3: Dendrogram of a cluster analysis of thermally modified wood. A (48h), B (9h), C (3h), D (1,5h), E (0h), F (18h), G (6h)

### Acetylated wood

Figure 4 presents NIR spectra of acetylated wood with increasing degree of acetylation (0% WPG – weight percentage gain up to 26,7% WPG). The increase of the WPG goes hand in hand with an increase of the bands at  $5950\text{ cm}^{-1}$  and  $5815\text{ cm}^{-1}$  (first overtone vibration of  $\text{CH}_3$  of acetyl groups of acetic acid esters) as well as the band at  $8547\text{ cm}^{-1}$  (second overtone vibration of  $\text{CH}_3$  of acetyl groups of acetic acid esters). The bands in the region of  $6880\text{ cm}^{-1}$  representing OH groups decrease as expected. The change of the spectra of sample with 0% WPG up to 26,7 % WPG clearly reflect the increasing degree of acetylation of OH groups.

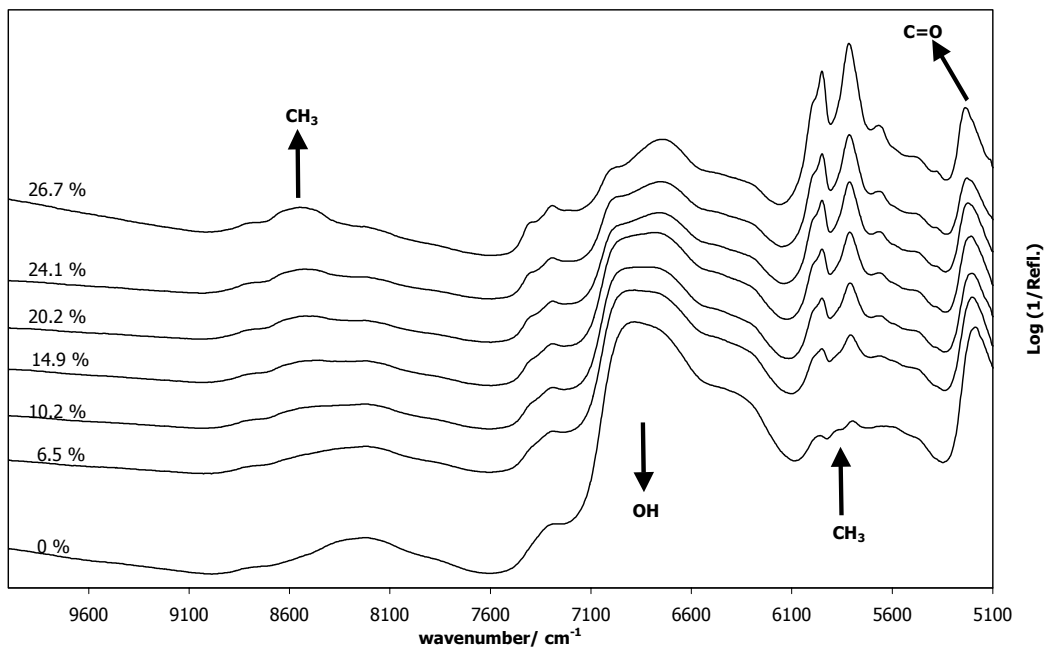


Figure 4: NIR – spectra of acetylated wood with increasing degree of acetylation (WPG %) from bottom to top

## CONCLUSIONS

It is shown that chemical changes of wood in consequence of thermal as well as chemical modification could be traced and classified respectively using NIR-spectroscopy. The use of second derivative and/or multivariate statistical methods was useful for following changes occurring on the wooden surface through the modification process. An easy classification possibility of different thermally treated samples is provided by means of cluster analysis. A further advantage of NIR spectroscopy is of course that it is easy to handle, provides data within a very short time, needs unsophisticated sample preparation and is cheap concerning the running costs.

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**ANALYSIS AND TESTING PROPERTIES**  
ORAL PRESENTATIONS





## Evaluation of Heat Treated Beech by Non-destructive Testing

Vincent Repellin<sup>1</sup>, René Guyonnet<sup>2</sup>

<sup>1</sup> Centre Spin, Ecole des Mines de Saint Etienne, 158 Cours Fauriel, 42 023 Saint Etienne, France  
repellin@emse.fr

<sup>2</sup> Centre Spin, Ecole des Mines de Saint Etienne, 158 Cours Fauriel, 42 023 Saint Etienne, France  
guyonnet@emse.fr

**Keywords:** Heat treatment, Wood stabilisation, retification®, Non Destructive Evaluation, free vibrations

### ABSTRACT

Improvement of dimensional stability and durability is desirable for the use of wood as a building material. For the last decade, retification® has been industrially developed. It consists in a stabilization and preservation of wood by heat treatment.

The aim of this study is to find simple and fast methods to characterise heat treated beech. Non destructive testing is expected to be relevant to evaluate the level of treatment and the properties for the use of heat treated wood.

Six treatments were carried out in a pilot reactor. The parameters of the retification® stage (temperature and time) were studied.

For each treatment, the non destructive tests (free oscillations in the fundamental mode, colour and dry weight loss) were performed, and the properties for use (mechanical resistance and volumetric shrinkage) measured.

Lightness and dry weight loss seem to be suitable properties to characterise beech retification® when the time parameter is fixed. However, they are not suitable for other wood species, and for retification stages of variable duration. Moreover, the correlation with the properties for use were plotted, but presented too large a dispersion to be relevant.

After correction of moisture content, the longitudinal Young's modulus of the material is slightly increased by each of the six treatments, but does not present any variation with changing parameters values. On the contrary, the mechanical resistance decreased with increasing temperature and time. Thus the dynamic Young's modulus is not reliable to evaluate the treatment and to predict the loss of mechanical resistance.

The logarithmic decrement was not increased by any of the treatments, which is in opposition with the hypothesis that retification® generates cracks and microcracks in the material.

Effects of long time at low temperature have been investigated. From these experiments, properties of treated wood may be improved significantly by choosing appropriate values of the parameters.

## INTRODUCTION

Improvement of dimensional stability and durability is desirable for the use of wood as a building material. For the last decade, stabilisation and preservation of wood by heat treatment have been industrially developed. Moreover, these heat treatments are more environmentally friendly than the chemical ones. Retification® is one of these heat treatments that stabilises wood and improves its durability. However, their main drawback is the loss of mechanical resistance of the material that happens at high temperature.

Some tests involving rather complicated physical or chemical techniques have been developed for the evaluation of the treatment. The first aim of this study is to find simple and fast methods that allow characterisation of the heat treatment of wood. Non destructive testing could easily fulfill these industrial requirements. But the considered properties have to vary significantly with the parameters of the retification stage (temperature and time), in spite of wood heterogeneity.

Six treatments have been carried out in a pilot reactor. The method was similar for all the treatments. The variable parameters were temperature (5 minutes at 200°C, 220°C, 240°C, and 260°C) and time (600 minutes at 200°C and 60 minutes at 220°C).

Properties related to the use of wood, such as the modulus of rupture (MOR) and the volumetric shrinkage have been measured.

Three types of non destructive tests have been performed. The measurement of CIE L\* a\* b\* colour and dry weight loss were studied. Nevertheless, the main efforts were focused on the free-free flexural vibrations test. Dynamic longitudinal Young's modulus (MOE) and logarithmic decrement were measured. These non destructive tests have been carried out before and after Retification®.

## MATERIALS PREPARATION

The purpose of this work was to investigate the influence of the two main parameters of retification® on the material : temperature and time of exposure. Six treatments were carried out in a pilot kiln, at the "Ecole Des Mines De Saint Etienne". This pilot kiln regulates by PID on the temperature of its atmosphere. The specimens were 85×85×25 millimetres beech beams, carefully cut in the longitudinal direction. Before heat treatment, the specimens had been held in a climatic chamber at 65% relative humidity 20°C. The moisture content (MC) of the specimens was 12%. Each batch was composed of sixteen specimens. The kiln is equipped with eight thermocouples that allow measurement of the temperature reached by the wood specimens.

Table 1 summarises the treatment parameters. The atmosphere was composed of nitrogen gas. The increase in temperature matched the standard one, used for the retification® process (Weiland 2000).

Four treatments were performed with a fixed time of exposure of 5 minutes. As the wood transformation is known to begin around 200°C, we chose the following temperatures : 200°C, 220°C, 240°C and 260°C. In order to investigate the effect of long exposure time at low temperatures of retification®, two treatments were carried out, at 200°C during 600 min and at 220°C during 60 min.

*Table 1: Experimental parameters of the treatments*

Treatment number	Temperature [°C]	Time [min]
1	200	5
2	220	5
3	240	5
4	260	5
5	220	60
6	200	600

For each treatment, non destructive tests (size, weight, colour and free vibrations) were performed before and after the treatment. After treatment, the specimens had been held until equilibrium in a climatic chamber at 65% relative humidity 20°C before being tested. The physical properties (volumetric shrinkage, MOR, and MC) of untreated and treated wood were measured by destructive methods. For each measurement, 48 samples were cut and tested.

## EXPERIMENTAL PROCEDURE

### *Evaluation of properties for use*

There are three main properties for the use of wood : mechanical resistance, volumetric shrinkage, and fungal resistance. In this work, we focused on the physical properties : mechanical resistance (evaluated by static bending) and volumetric shrinkage.

### **Mechanical resistance**

The bending strength of treated wood was measured using a four points bending device. 48 beams have been tested for each batch. The measurements were done following the French normative NF B 51-008. Normalised beams of dimension 20\*20\*360 mm underwent a force applied on the (LR) plane.

### **Volumetric shrinkage**

This test is carried out on cubic samples of around 2cm edge size. The volume of a cube is measured in the water saturated state and in the anhydrous state. The volumetric shrinkage is then calculated by the formula :

$$S = 100 \times \frac{V_s - V_0}{V_s} \quad (1)$$

where S is the volumetric shrinkage,  
 $V_s$  is the volume of the water saturated sample,  
 $V_0$  is the volume of the dried sample.

### *Evaluation by non destructive testing*

Non destructive evaluations can be done before and after the treatment. Consequently, they make some allowance for the natural variability of wood, and to measure only the modifications due to the heat treatment.

### **Colour**

The colour measurements were carried out using a MINOLTA Spectrophotometer CM-508i. The principle of colour measurement is inspired by the human vision. One colour is repaired in a three coordinate space. Thus, the device records three coordinates :  $L^*$  (also called lightness),  $a^*$ , and  $b^*$ . They match the three following pairs of colour : from white ( $L^*=100$ ) to black ( $L^*=0$ ), from red ( $a^*=+60$ ) to green ( $a^*=-60$ ) and from yellow ( $b^*=+60$ ) to blue ( $b^*=-60$ ). Thirty points were recorded on each specimen, before and after the heat treatment.

### Free oscillations

The vibrational properties were evaluated in the fundamental mode of free-free flexural vibrations. The impulse was given on the flat face of the specimens. The supports were placed at the nodal location of the first vibration mode. A piezoelectric captor recorded the vibration of the sample at the end of the beam (Fig. 1). Since the length of the specimens was ten times superior to their thickness, we could do the computation of the dynamic Young's modulus following the elementary Euler-Bernoulli's theory. Two quantities could be measured : dynamic MOE and logarithmic decrement.

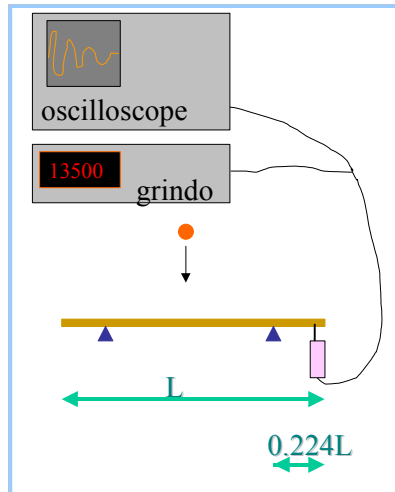


Figure 1: scheme of the device used to measure free oscillations.

The dynamic Young's modulus can be calculated from the following Eq. 2. It is linked to the stiffness of the material measured by static bending (Pellerin 1965).

$$E = \frac{48\pi^2}{(kL)^4} \frac{ML^3}{ba^3} f_i^2 \quad (2)$$

Where E is the dynamic modulus of elasticity in the longitudinal direction, M is the beam weight, L its length, a its thickness, and b its width.  $f_i$  is the natural frequency of vibration in the  $i^{\text{th}}$  mode, and  $kL$  is the solution of Eq. 3 matching the  $i^{\text{th}}$  mode of vibration. This Eq. 3 is worth in the case of free-free vibrations.

$$1 - \cos(kL)ch(kL) = 0 \quad (3)$$

Since we are working in the first mode we have :

$$E = 0,9464 \frac{ML^3}{ba^3} f_1^2 \quad (4)$$

or :

$$\frac{E}{\rho} = 0,9464 \frac{L^4}{a^2} f_1^2 \quad (5)$$

where  $E/\rho$  is the specific dynamic MOE and  $\rho$  is the specific gravity of the specimen.

As the specimens were cut in the longitudinal direction, we measured the Young's modulus in the longitudinal direction.

The logarithmic decrement gives an evaluation of the internal friction of the material. It is linked to the volumetric viscous damping force, which depends on the presence of defects, of microcracks and on the MC. From the experimental point of view, we measure the amplitude of

the  $N^{\text{th}}$  oscillation, and the amplitude of the  $(N+n)^{\text{th}}$  oscillation and calculate the logarithmic decrement following Eq. 6 :

$$\delta = \frac{1}{n} \ln \left( \frac{A_{\max N}}{A_{\max N+n}} \right) \quad (6)$$

Since the MOE and the logarithmic decrement should depend on the MC of the specimens, we fixed the correction relationships. In this purpose, four specimens of untreated beam were conditioned in a climatic chamber at different relative humidity. Their moisture content varied from 0 to 20% and we plot the logarithmic decrement and the specific dynamic MOE versus their MC. For the specific dynamic MOE, linear regression gave an average slope of  $-0.255$  GPa per percent of water. For the logarithmic decrement the linear regression gave an average slope of  $9 \cdot 10^{-4}$  per percent of water, but the data scattering was very large.

## RESULTS AND DISCUSSION

### *Properties for use*

Table 2 and Fig. 3 present the results of the tests.

The volumetric shrinkage decreases monotonically with increasing temperature and time of treatment. Indeed, the main effect of retification® is the destruction of the hemicelluloses (Weiland 2000), which are the most hydrophilic constituents of wood. Consequently, the wood is less sensitive to moisture.

*Table 2: Properties for use of treated and untreated beech*

Treatment number	Volumetric shrinkage S [%]	MOR [MPa]
Untreated	15.9 (1.4)	94.8 (15.8)
1	15.0 (1.4)	100.4 (24.9)
2	14.0 (1.0)	97.9 (21.1)
3	11.7 (1.8)	74.3 (19.3)
4	8.3 (1.2)	59.6 (21.0)
5	11.6 (1.2)	84.6 (18.7)
6	10.6 (1.5)	74.0 (25.6)

The mechanical resistance decreases from 240°C. This decay matches a degradation of the material. Since the modulus of elasticity is also a mechanical property, we expect that it should vary similarly than the MOR. Increasing time of treatment results also in a decrease of the volumetric shrinkage and the MOR.

### *Effect of temperature of treatment*

#### **Effect of the temperature on different properties**

The aim of this work is to find out properties easy to measure and that vary significantly with the level of treatment. For this purpose, a review of different properties of treated wood is presented in table 3. The colour (through the lightness  $L^*$ ) and the dry weight loss are the most influenced properties. They are already known to be relevant for the control of heat treatment of wood. Concerning the four treatment of five minutes, they both vary accurately with the temperature actually reached by the specimens (Fig. 2).

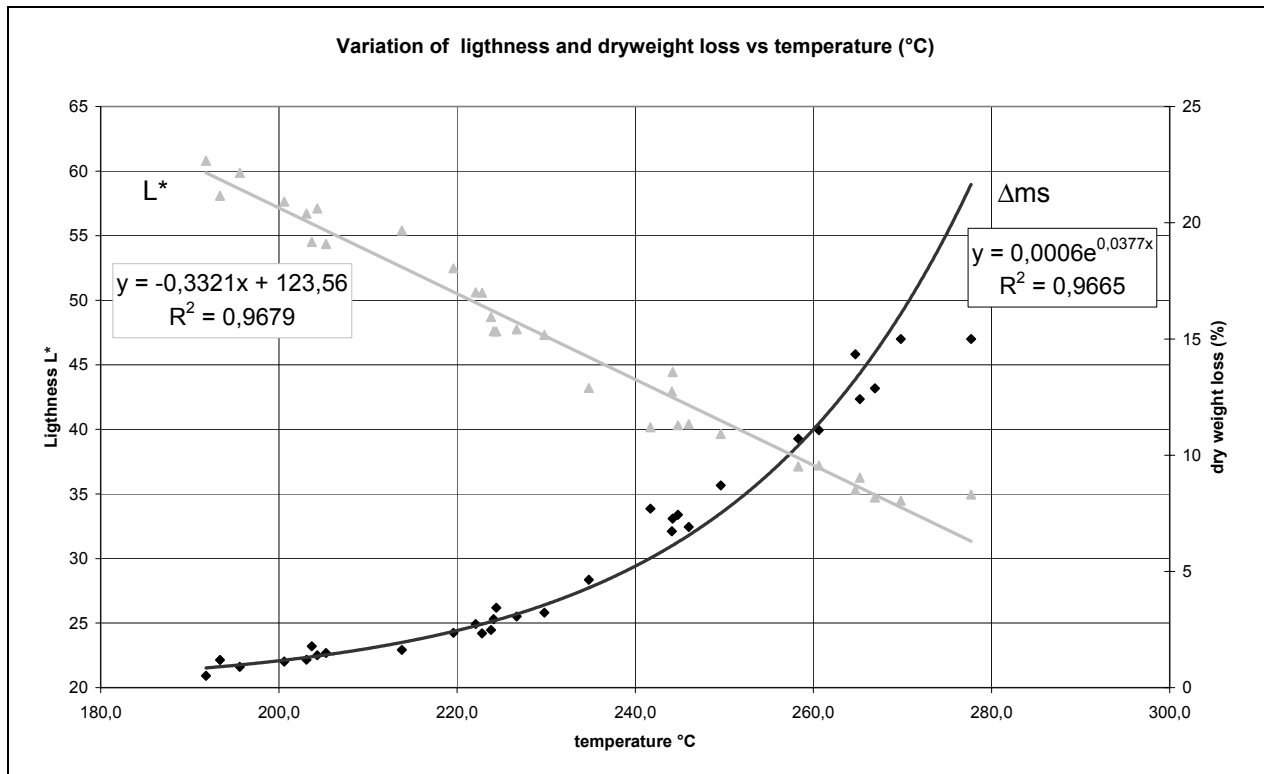


Figure 2: dry weight loss and lightness plot against the temperature reached by each beam of treatment 1, 2, 3 and 4.

Consequently, once the time of exposure is fixed, dry weight loss and lightness can be used to evaluate the retification® temperature. However, they cannot be used to evaluate both temperature and time of retification®. Indeed, treatments 5 and 6 result approximately in the same lightness and in the same dry weight loss as treatment 3, but they involve longer time.

Nevertheless, the dry weight loss should be used carefully. In this work it varies well with temperature, because beech is a broad leaved tree and does not contain resin. The weight loss of softwood is known to be unreliable as it depends on resin content. The use of colour also may not be relevant with all species of tree. Indeed, beech wood has a very homogeneous colour, which is not the case for all wood species.

Table 3: Results of non destructive tests

Treatment number	Dry weight loss Δms [%]	Equilibrium MC [%]	Colour : lightness L*	Colour : a*	Colour : b*
untreated	-	12.0 (0.3)	70.7 (3.5)	7.7 (0.7)	18.6 (1.2)
1	1.3 (0.3)	7.0 (0.8)	56.5 (2.2)	7.4 (0.6)	17.3 (0.6)
2	2.7 (0.7)	5.3 (0.5)	49.6 (2.9)	8.1 (0.4)	17.2 (0.9)
3	6.5 (1.7)	4.1 (0.7)	41.9 (2.9)	7.8 (0.5)	14.5 (1.4)
4	12.8 (1.9)	3.7 (0.3)	36.2 (2.1)	6.3 (0.7)	11.3 (1.6)
5	6.9 (1.6)	4.2 (0.5)	42.6 (2.3)	7.5 (0.3)	14.6 (1.2)
6	7.8 (0.8)	4.9 (0.5)	41.7 (1.9)	8.5 (0.5)	16.0 (1.2)

Moreover, correlation between the properties for use and lightness and dry weight loss were plotted, but presented too large dispersion to qualify the retification®. That is why we proposed to evaluate the relevance of the free oscillations method.

**Vibrational properties***Table 4: Vibrational properties of heat treated beech*

Treatment number	Ratio : ((Ed/ρ)treated )/ ((Ed/ρ)untreated )	Ratio : (δtreated )/ (δuntreated )
Natural	1 (0)	1 (0)
1	1.14 (0.06)	0.98 (0.10)
2	1.13 (0.07)	0.86 (0.07)
3	1.16 (0.02)	0.76 (0.09)
4	1.14 (0.02)	0.80 (0.07)
5	1.14 (0.02)	0.64 (0.09)
6	1.13 (0.02)	0.85 (0.08)

There are two observations concerning the specific dynamic Young's modulus (Table 4):

- it increases from natural to treated state,
- there is no obvious variation following the parameters.

To conclude, it is not possible to evaluate the treatment with this property.

The logarithmic decrement decreases with increasing temperature of treatment from 200°C to 240°C. But the scattering of the data is so large that it is again impossible to quantify the heat treatment with this property. By destruction of the hemicellulose, heat treatment makes the wood lose its affinity for water. As a consequence, viscous damping is reduced and the logarithmic decrement decreases. Moreover, the stress strain curves of the high temperature batch (treatment 3 and 4) have the shape of a brittle material. The heat treated wood behaves more like a brittle material progressively with increasing values of the parameters.

During retification®, two phenomena may influence the vibrational properties : loss of MC (which increases the MOE and decreases the logarithmic decrement), and lignocellulosic material modification. In order to investigate the influence of the material modification on the vibrational properties alone, it was necessary to calculate and to eliminate the influence of the MC.

**Correction of the vibrational properties with MC**

We know that the equilibrium MC of the treated wood decreases with increasing temperature and time of treatment (Table 3). Consequently, we had to do the correction of the vibrational properties values according to the variation in moisture content. Linear regression of the specific dynamic MOE of untreated wood vs. MC between 0% and 20% was plotted. For each batch, one could then compute the specific dynamic MOE of untreated wood at the same moisture content as the equilibrium moisture content of the treated wood ((Ed/ρ)untreatedcor). The ratio ((Ed/ρ)treated)/((Ed/ρ)untreatedcor) so calculated (Table 5) allows comparison of the natural and treated wood at the same moisture content.

Once the correction is carried out, one observes that the MOE of wood is slightly enhanced by each of the treatments. We can conclude from this, that the modification of material results in an increase of the Young's modulus. Phenomena involved in this modification are discussed. As well as before correction, the scattering of the increase is large, which prevents comparison between treatments of different parameters.

The same correction in MC was done for the logarithmic decrement. Considering the values obtained and the scattering of the data, no obvious difference between the decrement of anhydrous wood and the decrement of treated wood was observed.



**Table 5: Corrected vibrational properties of heat treated beech**

Treatment number	Ratio : ((Ed/ρ) <sub>treated</sub> )/ ((Ed/ρ) <sub>untreated cor</sub> )	Ratio : (δ <sub>treated</sub> )/ (δ <sub>untreated cor</sub> )
1	1.07 (0.06)	1.12 (0.13)
2	1.04 (0.02)	1.00 (0.10)
3	1.04 (0.02)	0.90 (0.12)
4	1.02 (0.01)	1.00 (0.10)
5	1.04 (0.02)	0.77 (0.12)
6	1.04 (0.01)	1.03 (0.11)

We can conclude from this, that the measurement of the vibrational properties in the fundamental mode is not relevant to make an evaluation of the retification® of beech beams.

### **Mechanical and vibrational properties**

Another point concerns the mechanical resistance of the treated wood. The bending strength decreases significantly from 240°C (Table 4). During the heat treatment, physical and chemical transformations of the material lead to a loss of mechanical resistance. In the spite of this, the specific Young's modulus is not modified from 200°C until 260°C. Thus, the material degradation causes reduction of mechanical resistance, but no variation of the modulus of elasticity.

The longitudinal MOE of a beam depends strongly on the microfibril angle of the S2 layer, and depends less strongly on the crystallinity of cellulose and stiffness of the amorphous matrix (Ono, Norimoto 1983). These three elements of the wood structure could be slightly influenced by the heat treatment and result in this slight increase of the Young's modulus.

The mechanical strength of wood is more linked to the presence of cracks, and their opportunity of initiation and propagation. Thus, the loss of mechanical resistance may be attributed to a higher number of cracks and microcracks in the treated material, or/and to a decrease of the energy necessary for a crack to initiate and propagate in the material.

With a microscopic investigation of the microstructure, no obvious damage is visible on heat treated wood (Avat 1993). Moreover, since the logarithmic decrement is decreased by heat treatment (or at least not increased once the moisture correction is done), the hypothesis of a higher number of microcracks in the treated beech should be rejected. Indeed, the presence of more microcracks should lead to a higher internal friction, and thus to an increase of the logarithmic decrement.

As a conclusion, more investigation is necessary to find out the influence of the retification® on the structure and microstructure of the wood, and to do the link with the macroscopic properties as mechanical resistance and vibrational properties.

### ***Effect of long treatment time***

The last point of the study was the effect of long treatment time. Treatments number 5 and 6 were performed (Fig.3) and (Table 2). One of the benefits of long treatment time at low temperatures, is that the conduct of the process is easier. Indeed, no exothermic effect is expected and the temperature homogeneity is better in the pilot kiln. Moreover, a lot of reaction is involved during retification® (Bohnke 1993, Weiland 2000). By choosing low temperature

and long time treatment, one tends to improve reactions that decrease volumetric shrinkage, and to slow reactions that decrease the MOR.

Treatment 5 and 6 result both in a decrease of the volumetric shrinkage and in a loss of the mechanical resistance. It seems to be difficult to get a reduction of volumetric shrinkage without reduction of the bending strength. In the spite of this general observation, there is no evidence that these two effects are caused by the same reactions ; and we may find an optimum of the parameters values, where the mechanical loss would be reduced.

Concerning the volumetric shrinkage, a one hour retification stage at 220°C (batch number 5) allowed to reach the same level of stabilisation as a five minutes treatment at 240°C (batch number 3). The mechanical resistance seem to be slightly less reduced, but the dispersion of MOR is large. Nevertheless, the difference on average MOR between number 3 and 5 is statistically significant at risk 2%.

Since this difference is statistically significant, we expect that an optimum of the parameters exists to get the best compromise for the use properties. Moreover, comparing treatment 6 and 3, the volumetric shrinkage is lower for treatment 6 with approximately the same value of MOR.

According to these observations, reactions that improve the reduction of volumetric shrinkage should prevail at low temperature (until 220°C) with regard to reactions that cause mechanical degradation. Though, more investigation is necessary to find out what reaction occurs at a given temperature.

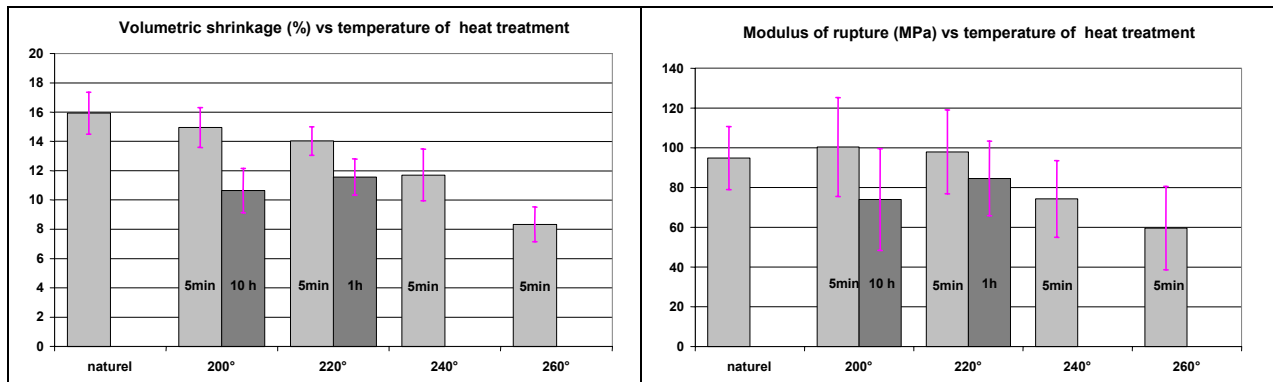


Figure 3: properties for use of retified® beech.

## CONCLUSIONS

Six treatments have been carried out in a pilot reactor. The parameters of the retification® stage (temperature and time) have been studied.

For each treatment, the non destructive tests (free oscillations in the fundamental mode, colour and dry weight loss) were performed, and the properties for use (mechanical resistance and volumetric shrinkage) measured.

Lightness and dry weight loss seem to be suitable properties to characterise beech retification® when the time parameter is fixed. However, they are not suitable for other wood species, and for retification stages with a variable duration. Moreover, the correlation with the properties for use were plotted, but presented too large a dispersion to be relevant.

After correction of moisture content, the longitudinal Young's modulus of the material is slightly increased by each of the six treatments, but does not present any variation with changing parameter values. On the contrary, the mechanical resistance decreased with increasing temperature and time. Thus the dynamic Young's modulus is not reliable to evaluate the treatment and to predict the loss of mechanical resistance.

The logarithmic decrement presented a large dispersion, which does not allow to quantify retification® with this property. After moisture correction, it was not increased by any of the treatments. This observation is in opposition with the hypothesis that retification® generates cracks and microcracks in the material.

Effects of long treatment time at low temperature have been investigated. From these experiments, it is concluded that significant improvement of the wood properties may be expected by choosing appropriate values of the parameters.

More investigation is required to find out what reaction prevails according to the temperature, and to understand better the mechanisms that cause the loss of mechanical resistance.

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## Acetyl Content Determination using Different Analytical Techniques

E.P.J. Beckers<sup>1</sup>, H.P.M. Bongers<sup>2</sup>, M.E. van der Zee<sup>3</sup>, C. Sander<sup>4</sup>

<sup>1</sup> SHR Timber Research, PO Box 497, 6700 AL, Wageningen, the Netherlands, e.beckers@shr.nl

<sup>2</sup> SHR Timber Research, PO Box 497, 6700 AL, Wageningen, the Netherlands, f.bongers@shr.nl

<sup>3</sup> SHR Timber Research, PO Box 497, 6700 AL, Wageningen, the Netherlands, m.vanderzee@shr.nl

<sup>4</sup> Rinntech, Bierhelderweg 20, 69126 Heidelberg, Germany, constantin.sander@rinntech.de

**Keywords:** acetylation, acetyl content, titration, HPLC, FTIR, autofluorescence, ToF-SIMS

### ABSTRACT

Acetylation has been shown to improve certain wood properties considerably. However, the degree of improvement of all these properties has a direct correlation with the degree of acetylation. It is therefore very important that this is determined prior to selling the acetylated wood. This requires a fast and reliable analysis in order to do so. Furthermore, when solid wood of larger dimension is treated, process conditions can result in a gradient in degree of modification within a cross section. The use of an increase in weight (WPG) as a value for the degree of modification is not suitable then, because it requires an oven-dry weight before and after treatment. Several analytical techniques were evaluated in their ability to determine the proper degree of acetylation. They included titration, high performance liquid chromatography (HPLC), infrared (FTIR), autofluorescence and Secondary Ion Mass spectroscopy (ToF-SIMS). The results were based upon research on solid wood modification at SHR during the past decade. Results of the different techniques were correlated to one another. The autofluorescence analysis had a correlation with the sample moisture content and not directly to the degree of acetylation. HPLC, titration and FTIR-KBr gave good and repeatable results. All these analyses took at least several hours and were quite labour intensive, mainly due to the sample preparation. Neither of them could be done without destroying at least part of the wood. The ToF-SIMS analysis can be done on (pieces of) solid wood, but it requires expensive equipment and only preliminary data were obtained. An FTIR analysis using an ATR device could be suitable for a fast and indicative determination of acetylated wood. When the actual degree of acetylation is required, one of the more labour intensive and time consuming, but more accurate analytical techniques should be used. More work will be done on a colouring agent which would be the preferred (fast) technique.

### INTRODUCTION

Research on the modification of wood has intensified the past decade which has led to a (near) commercialisation of some of these techniques, especially thermal treatments. Of all chemical modifications, the acetylation of wood has been studied most intensively. Apart from acetylation of smaller wood particles (*e.g.* fibres, particles, chips) efforts have been made to acetylate solid wood and to develop a process that is commercially viable. This mainly depends on the eventual costs of the process. Material properties of the acetylated wood are not an obstacle. The treatment has shown to result in a very durable, dimensionally stable and UV-resistant material with all mechanical properties of the untreated wood maintained (Beckers *et al.* 1998, Beckers and Militz 1994, Beckers *et al.* 1994, Goldstein *et al.* 1961, Larsson and Simonson 1994, Larsson-Brelid *et al.* 2000, Militz 1991, Rowell *et al.* 1989, Singh *et al.* 1992).

However, the degree of improvement of all these properties has a direct correlation with the degree of acetylation. It is therefore very important that this is determined prior to selling the acetylated wood. This requires a fast and reliable analysis in order to do so. When acetylating solid wood an additional issue is raised. For many wood modification processes, especially acetylation, the increase in weight (WPG) is used as a value for the degree of modification. It is measured by determining the oven dry weight of a sample before and after treatment (Eq. 1). However, when solid wood of larger dimension is treated, process conditions can result in a gradient in degree of modification within a cross section. Determination of the oven dry weight of wood blocks with large (cross sectional) dimensions prior to treatment can only be determined indirectly by measuring the moisture content and weight of the whole sample. Drying the samples to 0% moisture content (m.c.) is not possible without destroying the wood (cracks). A more direct determination of the degree of acetylation therefore is required.

$$WPG = \left( \frac{M_1 - M_0}{M_0} \right) * 100 \text{ [%]} \quad (1)$$

whereas:

$M_0$  = oven-dry weight before acetylation [g]  
 $M_1$  = oven-dry weight after acetylation [g]

The degree of acetylation is directly correlated to the amount of substituted hydroxyl groups. During the process these groups are substituted by acetyl groups. A chemical analysis of the acetyl content by High Performance Liquid Chromatography (HPLC) is used by several research groups. In this research this analytical technique as well as several others have been evaluated in their ease of use and ability to determine the proper degree of acetylation.

Furthermore, preparation of samples prior to analysis was evaluated as well. Acetic acid formed during the treatment and unreacted acetic anhydride have to be removed prior to analysis of the acetyl content. A residual amount would result in a higher content of acetate after saponification, the latter one being required for many chemical analyses. This would result in inaccurate data. During these preparations not all acetic acid might be removed or even acetyl groups could be lost. Therefore a comparison was made between three different ways of removing acetic acid and anhydride.

## EXPERIMENTAL METHODS

The results mentioned in this paper are based upon research on solid wood modification at SHR during the past decade. Wood species, dimensions, acetylation processes and even equipment varied during that period. All treatments though were done using uncatalysed acetic anhydride. For all analyses mentioned underneath acetylated solid wood (irrespective of treatment) was used as a material source.

### **Sample preparation**

Three different methods were used to remove unreacted acetic anhydride and by-product acetic acid from poplar samples prior to titration and HPLC analysis:

1. impregnation with water, leave overnight at room temperature, oven drying ( $103 \pm 2$  °C), sampling, grinding
2. grinding, rinsing with water, air drying for 10 days
3. impregnation with water, leaching according to EN 84, oven drying, grinding

For most analytical techniques, the sample size of the wood needs to be reduced. After drying, the solid wood blocks therefore were cut into smaller pieces or particles. These particles were then ground into wood flour using a Retsch ZM100. For most analyses, a sieve with 250 µm perforations was used. To determine the influence of particle size in the FTIR-KBr-tablet technique a sieve with 125 µm perforations was used as well.

### **Titration**

Determination of the acetyl content of wood using titration was performed using the Eberstadt method (Goldstein *et al.* 1961), which is based upon ASTM D871-56. The acetyl gain was calculated according to Eq. 2. The top layer of the samples (C) as well as the centre part of the sample (A) and the section in between (B) were analysed separately. Results were compared to those obtained by HPLC analysis.

$$\text{Acetyl gain} = \left[ \frac{M \cdot (10 \cdot N_2 - T_{ac} \cdot N_1)}{10^3 \cdot m_{ac}} - \frac{M \cdot (10 \cdot N_2 - T_{un} \cdot N_1)}{10^2 \cdot m_{un}} \right] \cdot 100 [\%] \quad (2)$$

whereas:

- $M$  = mol mass acetyl group (43 g/mol)
- $m$  = amount of wood flour [g]
- $T$  = required amount of hydrochloric acid [ml] after titration
- $N_1$  = normality of hydrochloric acid solution (0.1)
- $N_2$  = normality of sodium hydroxide solution (1.0)
- $ac$  = acetylated wood
- $un$  = untreated wood

### **High Performance Liquid Chromatography (HPLC)**

Approximately 1 g of refined wood flour was weighed into a clean and dry glass beaker. After drying for 4 h in an oven at 103±2 °C the exact amount of wood flour was registered. Subsequently 0.1 g of sodium butyrate was added as an internal standard. All weights were recorded to mg accuracy. The wood flour was stirred after adding 100 ml of 0.2 M sodium hydroxide and a vacuum was applied for 30 min. This mixture was left overnight (18 h) at room temperature for saponification. The mixture was then filtered using a paper filter. Approximately 2 ml of the remaining liquid was put into an autosampler after additional membrane filtering (0.45µm).

Further analysis was done on a TSP SpectraSERIES HPLC with data collector and integrator. An ion exchange column " (Aminex HPX87H, 300 mm x 7.8 mm) was used with an eluent of 0.005 M sulphuric acid (membrane filtered and ultrasonicated under vacuum) at 0.8 ml/min and a 10 µl injection volume. Detection was done at 210 nm. For each analysis, a standard series of four different concentrations of sodium acetate (400 to 2400 ppm) and sodium butyrate was added. Comparable to the saponification of the wood flour, a 0.2 M sodium hydroxide solution was used. The acetyl content compared to oven-dry weight is calculated according Eq. 3.

$$\text{Acetyl} = \frac{m_1}{m_2} \cdot \frac{43}{59} \cdot 100 [\%] \quad (3)$$

whereas:

- $m_1$  = weight of acetate determined by HPLC [g]
- $m_2$  = weight of oven-dried wood [g]
- 43/59 = correction for molecular weight acetyl / molecular weight acetate

### ***Fourier Transform Infrared (FTIR)***

#### **Potassium bromide tablets (FTIR – KBr)**

Dried acetylated wood flour (5 mg) and 2 g of potassium bromide (KBr) was ground in an agate mortar. Portions of 350 mg of this mixture were dried overnight in an oven of  $103 \pm 2$  °C and pressed into tablets. Directly after producing the tablet, it was analysed to avoid absorption of moisture. Every tenth measurement was a blank KBr tablet. For each run, 32 scans (absorbance spectra) were made using a BioRad FTS165 spectrometer with a resolution of  $8 \text{ cm}^{-1}$ . A base line correction was made by setting the lowest point between  $2000 \text{ cm}^{-1}$  and  $1800 \text{ cm}^{-1}$  to a zero absorbance. The absorbance intensity of the individual peaks was done with the integration programme Quantbasic for gram/386 (BioRad). To determine the degree of acetylation the peak at  $1740 \text{ cm}^{-1}$  (C=O stretch) was correlated to highest peak around  $1510 \text{ cm}^{-1}$  (C=C stretch) taking into account that the benzene ring vibration in lignin does not change during the acetylation. In further research the  $1740 \text{ cm}^{-1}$  was correlated to the C-O stretch in cellulose and hemicellulose ( $1060 \text{ cm}^{-1}$  and  $1010 \text{ cm}^{-1}$ ). Results were compared to those obtained by HPLC analysis. FTIR analyses were also used to check whether the saponification during sample preparation was complete.

#### **Attenuated Total internal Reflection geometry (FTIR-ATR)**

A small piece of acetylated wood was cut from a larger sample. An infra red analysis was made using an attenuated total internal reflection geometry device (ATR). It consists of a glass plate to which a small piece of sample can be pressed on for analysis. By several mirrors the laser beam is directed to the sample and reflected to the analytical sensor. An analysis was made of several degrees of acetylation on both the transversal and cross cut side of the sample. Based on these results a larger amount of samples with similar degrees of acetylation was analysed. Results were compared to those obtained by HPLC analysis.

### ***Autofluorescence***

Fluorescence microscopy was performed with unstained thin sections of wood ( $20 \mu\text{m}$ ), which were mounted in glycerine. Digital images were taken using an Olympus fluorescence microscope with 60x (dry) and 100x (oil immersion) objectives respectively. Excitation was performed with band pass filtered UV-light of 360-370 nm wavelength (beam splitter at 400 nm). The fluorescence emission was then imaged after passing through a low pass filter ( $> 420 \text{ nm}$ ).

Acetylated Norway spruce (32), Scots pine (36) and beech (33) samples of  $40 \text{ mm} \times 40 \text{ mm} \times 5 \text{ mm}$  (r x t x l) were conditioned at  $20$  °C and 65% RH. Measurements within the latewood tissue were performed on planed cross-sectional surfaces of the samples using a Leitz fluorescence microscope with incident illumination and a 10x objective. Samples were irradiated on an area of  $18 \times 18 \mu\text{m}$  with Ploem incident UV-light (1100 V). The excitation wavelength of 365 nm was set via an interference filter (maximum aberration: 5 nm). This wavelength secures an even excitation of all lignin molecules (Frey-Wissling, 1964). The fluorescence emission was recorded through a RCA c 31014 photomultiplier and a Goerz RE 541 recorder.

The fluorescence emission spectrum and the intensity of the fluorescence maximum were recorded for each sample. Ten measurements at the maximum emission wavelength were taken over the whole sample, since each measurement covered a small area only and inhomogeneity of acetylation might lead to non-typical results with just one measurement.

**Time of Flight Secondary Ion Mass Spectroscopy (ToF-SIMS)**

Secondary ions mass spectrometry is primarily based on the fact that bombardment of surfaces by ions of a few KeV energy not only leads to the emission of elements but also to the emission of intact involatile molecules which are characteristic of the chemical composition in the uppermost monolayer of the surface. These secondary ions can be either positively or negatively charged, depending on their electron configuration in the outermost electron shell. The acetylation analysis was carried out in negative mode analysis. These secondary ions are collected and analyzed by Time of Flight on their mass and intensity using standard mass spectrometry techniques. These intensities per mass can be used either to make a mass spectrum (large surface – general modification level) or an image (modification on cellular level). (Adriaens *et al.* 1999, Hagenhoff 2000, Vaeck *et al.* 1999).

Scots pine sapwood samples of 10 mm x 10 mm x 10 mm (r x t x l), were treated to a high degree of acetylation (> 20%) in a glass laboratory 1 l reactor. These samples were then planed by microtome in order to get a very smooth surface This was one of the requirements for further ToF-SIMS analysis. A spectrum was made to determine whether a difference could be observed between untreated and acetylated wood. Based on these results three more batches of Scots pine sapwood samples (10-mm x 10-mm x 25 mm - r x t x l) were acetylated to a WPG of 4.6, 9.7 and 18.6%. Since in the previous samples interference of silicon oil was detected, a vacuum during these batches was applies without the use of silicon grease. The three different acetylation levels were obtained by extracting samples from the reacting medium at successive time intervals. After acetylation, all samples were post treated to remove residual acetic acid. After conditioning, the samples were boiled in water in order to be able to slice them very smooth in the microtome at the crosscut surface. They were finally sent to TASCAN GmbH in Münster (Germany) for ToF-SIMS analyses.

**RESULTS AND DISCUSSION****WPG vs. HPLC**

Acetylation is a single site reaction which means that one molecule of acetic anhydride reacts with one hydroxyl group without polymerisation. This means that the complete acetyl weight gain can be used to determine the amount of substituted hydroxyl groups or weight gain (Eq. 4 or 5). The correlation between acetyl content determined by HPLC and WPG is shown in figure 1. These results are only valid for Scots pine sapwood because the natural acetyl content has to be subtracted from the acetyl content of the acetylated wood and the natural acetyl content differs for each wood species.

$$WPG_t = \frac{Ac_{tot} - Ac_0}{1 - 0.01 * Ac_{tot}} [\%] \quad (4)$$

or:

$$Ac_{tot} = \frac{WPG + Ac_0}{1 + 0.01 * WPG} [\%] \quad (5)$$

whereas:

$WPG_t$  = theoretical weight gain [%]

$Ac_{tot}$  = total acetyl content [%]

$Ac_0$  = acetyl content of untreated wood [%]



The theoretical weight gain (Fig. 4) will differ from the actual weight gain. A loss of extractives might occur during acetylation for which the WPG must be corrected (Goldstein *et al.* 1961). This differs for each wood species. Furthermore, it is unknown which substances will be extracted with acetic anhydride or acid and what influence temperature has on this process. It will also be very likely that certain extractives will be acetylated themselves and as a result (a proportion) cannot be extracted any more. They do contribute though, to a weight gain of the wood but have no effect on material properties such as dimensional stability. For scientific research, wood extractives can be removed prior to treatment but for commercial acetylation of solid wood normally kiln dried timber will be used. The loss of extractives though seems to be minimal during acetylation. The correlation between WPG and acetyl *gain* (Fig. 3) is more or less independent from the wood species.

### **Titration**

A comparison of the degree of acetylation determined by titration and HPLC is shown in table 1. The absolute acetyl content determined by titration was higher compared to that obtained by HPLC analysis. During titration other wood components probably reacted with the added sodium hydroxide and accounted for a higher titre of the hydrochloric acid. The acetyl gain though is quite similar for both methods.

Only slight differences occur between the various ways to remove residual acetic acid.

**Table 1: Acetyl content determined by titration (with three different sample preparations) and HPLC**

Location in the sample:	Sample preparation method			Average	HPLC	
	1	2	3		%Ac	$\Delta\%Ac$
	%Ac			$\Delta\%Ac$	%Ac	$\Delta\%Ac$
Untreated				5.0	2.6	
Outer layer	12.6	13.3	12.9	12.9	10.3	7.7
Inner section	13.6	13.4	14.0	13.7	11.2	8.6
Centre	14.8	15.0	15.6	15.1	12.4	9.8

### **FTIR-KBr**

Results in figure 4 show that saponification during sample preparation has been complete. The correlation between a FTIR-analysis using KBr tablets and HPLC analysis of the acetyl content is shown in figures 5 to 10.

Results in figures 5-8 show that grinding the wood flour to smaller particles (250 vs 125  $\mu\text{m}$ ) has hardly any influence on the results for soft wood species. In hardwood species though results are quite different, especially for beech.

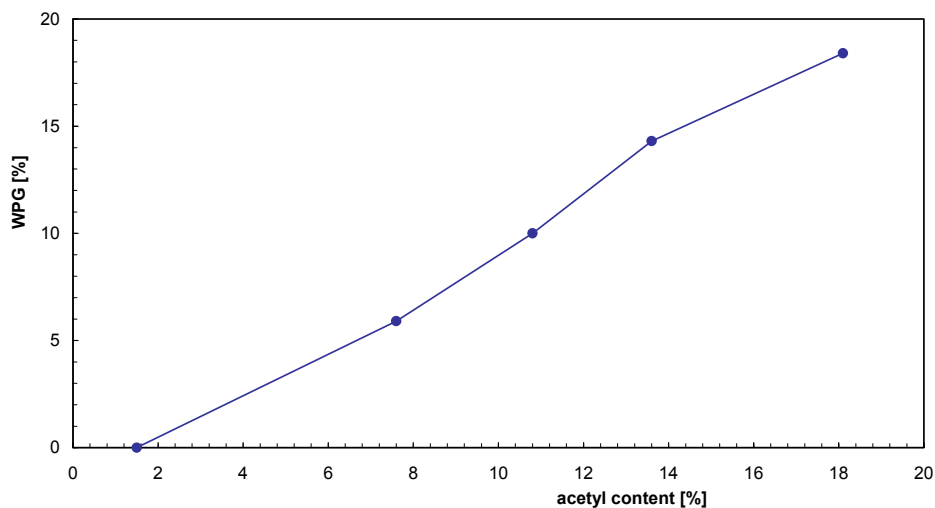
The  $1740\text{ cm}^{-1}/1060\text{ cm}^{-1}$  ratio shows a better correlation to the acetyl content determined by HPLC compared to the  $1740\text{ cm}^{-1}/1510\text{ cm}^{-1}$  ratio. When modifying wood with acetic anhydride mainly lignin is acetylated (Rowell *et al.* 1994) while the crystalline cellulose fibres are hardly accessible for modification. The C=C stretch in the aromatic ring of lignin could therefore be influenced or altered by the attached acetyl groups. The structure of the cellulose polymers on the other hand will stay the same, which results in a constant C-O stretch before and after acetylation.

### **FTIR-ATR**

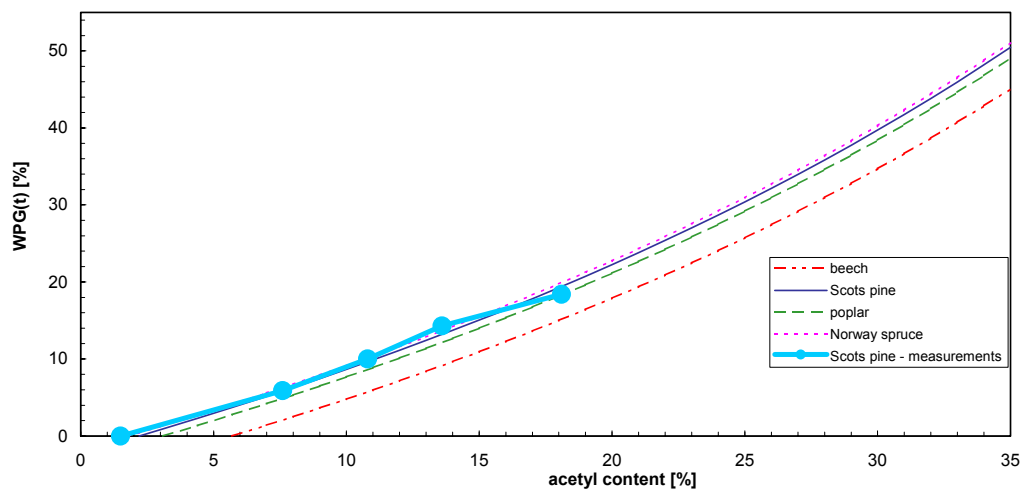
Results of the FTIR-ATR are shown in figures 11 to 14. Measuring the transverse side gives a better correlation to the acetyl content determined by HPLC, compared to a measurement of the

cross-cut side. Analysing the latter one involves a much smaller amount of cell wall material on an equal surface. This will probably have contributed to the large variation in results. A comparison between FTIR-ATR and HPLC analysis gave a good linear correlation for both earlywood ( $r^2 = 0.94$ ) and latewood ( $r^2 = 0.98$ ). The differences between earlywood and latewood were minimal. Further analyses were therefore done on the transverse side of wood blocks with no distinction between earlywood and latewood.

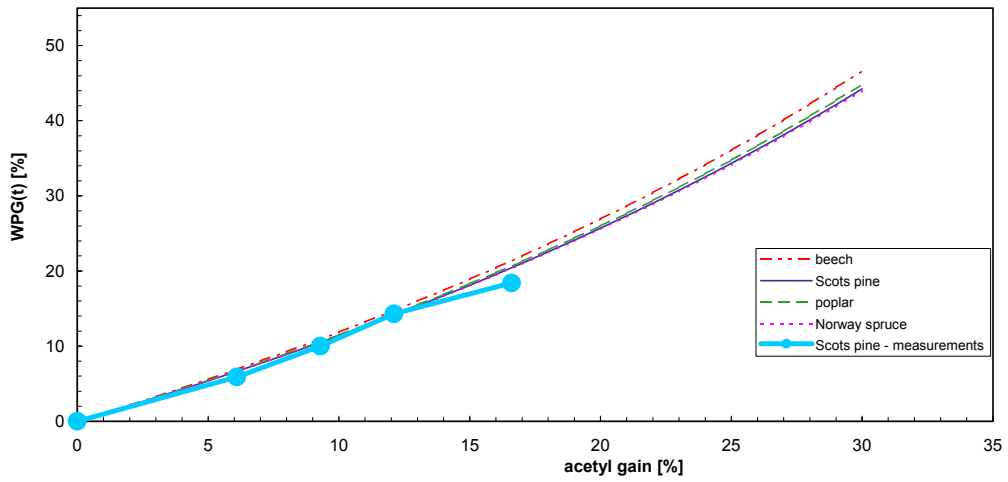
Results after analysing a large amount of samples show that a very precise determination of the degree of acetylation is not possible using FTIR-ATR. An FTIR ratio of 3.0 could both be an acetyl content of 22% or 28%, with clearly different wood properties. An acetyl content of 22% on the other hand results in an FTIR ratio varying from 1.8 to 3.5. A distinction between an acetyl content of 2, 10 or 20% is possible though. The main advantage of the developed method is its fast and less time consuming nature, since measurements can be performed on wood blocks and do not need to be saponified prior to analysis (*i.e.* HPLC-method). No mixture of wood flour is made though, comparable to the FTIR-KBr or HPLC. The surface which is measured is relatively small, which means that either wood rays, S1-layer or middle lamella can be measured with a difference in lignin content. A larger amount of samples therefore needs to be analysed (> 10). An average of those values gives a good correlation ( $r^2 > 0.9$ ) to an HPLC analysis.



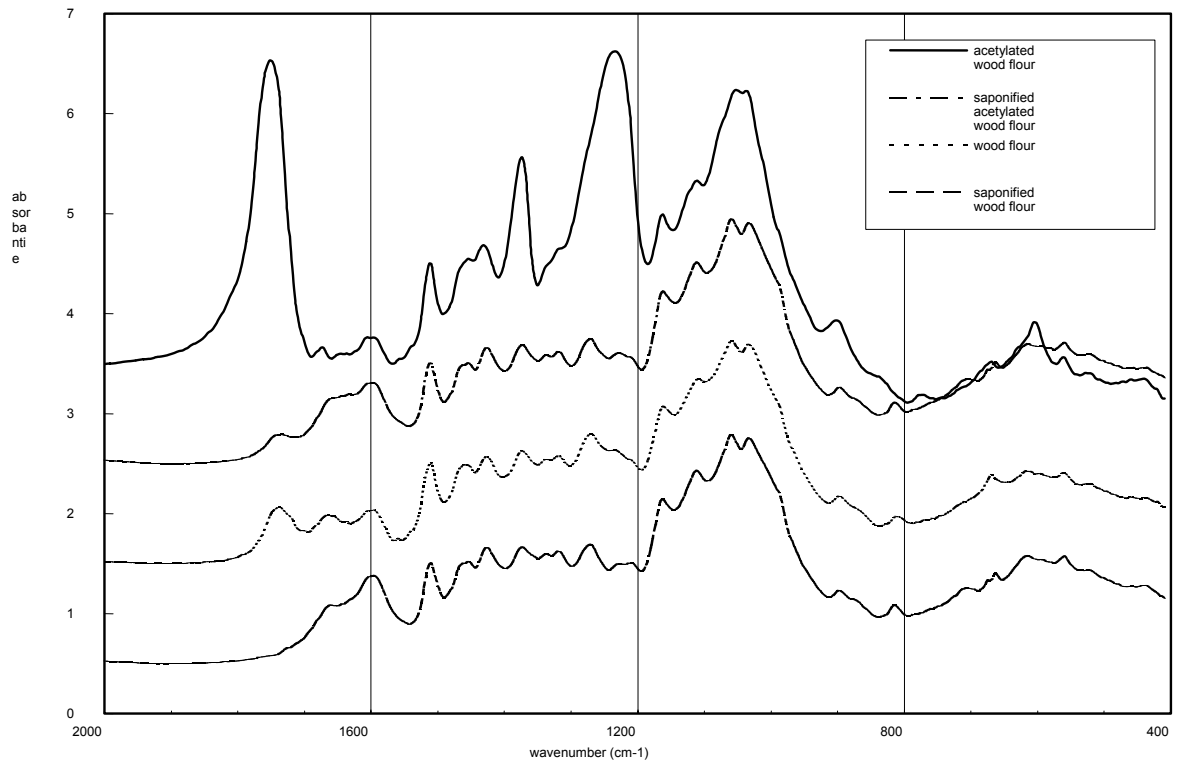
**Figure 1: Correlation between acetyl content and weight percent gain of acetylated Scots pine sapwood**



**Figure 2: Theoretical weight percent gain correlated to acetyl content for acetylated beech, Scots pine sapwood, poplar and Norway spruce**



**Figure 3: Theoretical weight percent gain correlated to acetyl gain for acetylated beech, Scots pine sapwood, poplar and Norway spruce**



**Figure 4: Infra red spectra of untreated and acetylated Scots pine sapwood wood flour before and after saponification.**

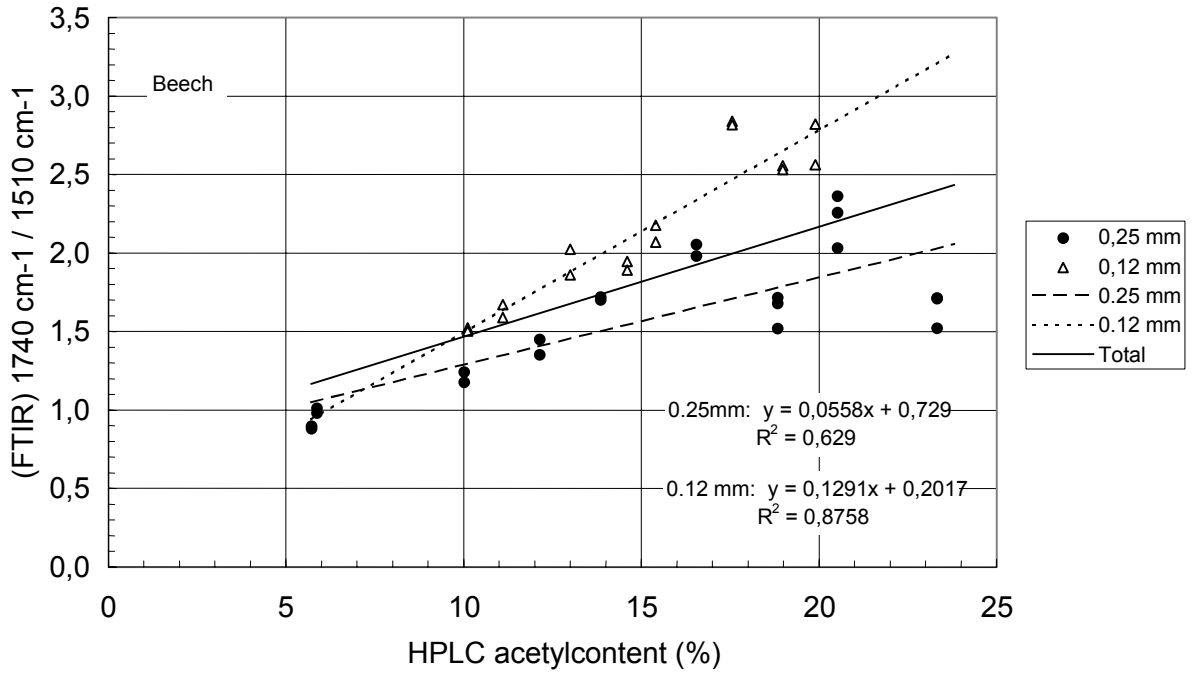


Figure 5: Correlation between FTIR and HPLC acetyl content of acetylated beech of various grinding sizes during sample preparation

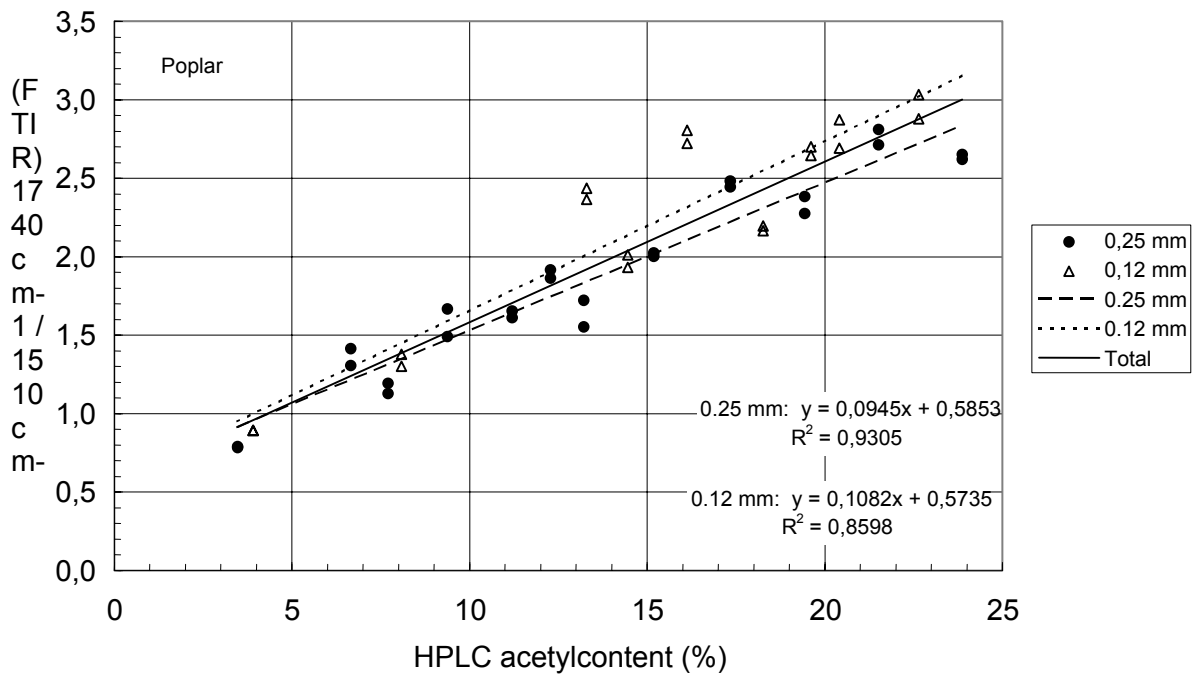


Figure 6: Correlation between FTIR and HPLC acetyl content of acetylated poplar of various grinding sizes during sample preparation

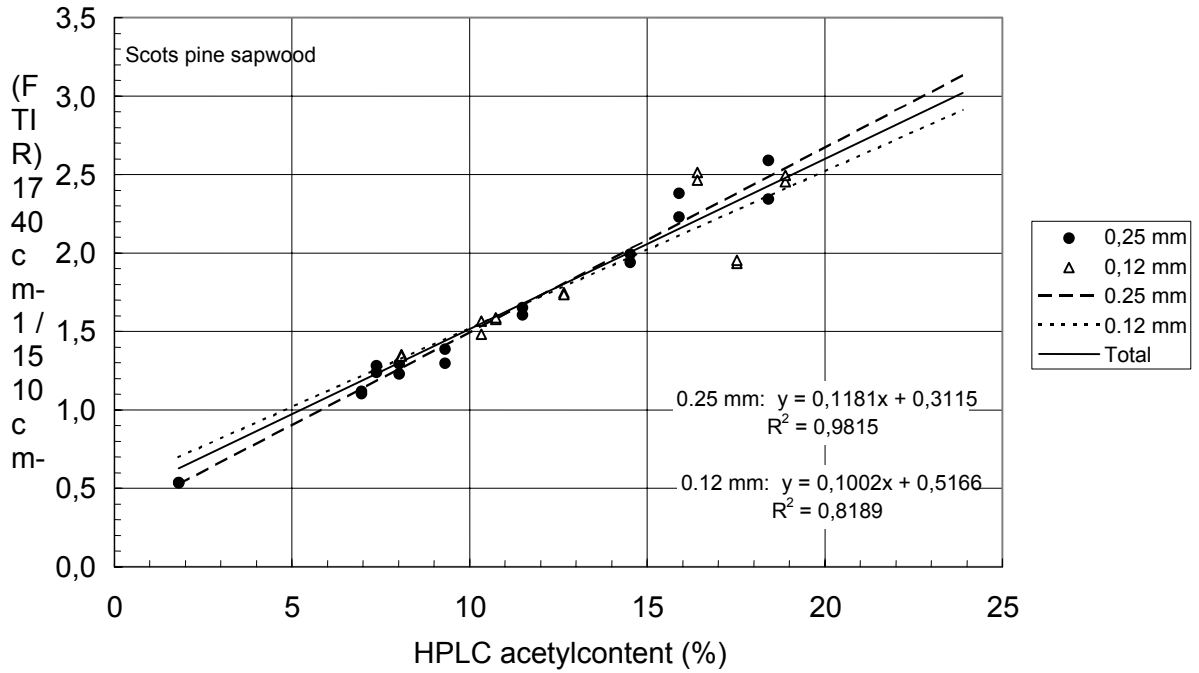


Figure 7: Correlation between FTIR and HPLC acetyl content of acetylated Scots pine sapwood of various grinding sizes during sample preparation

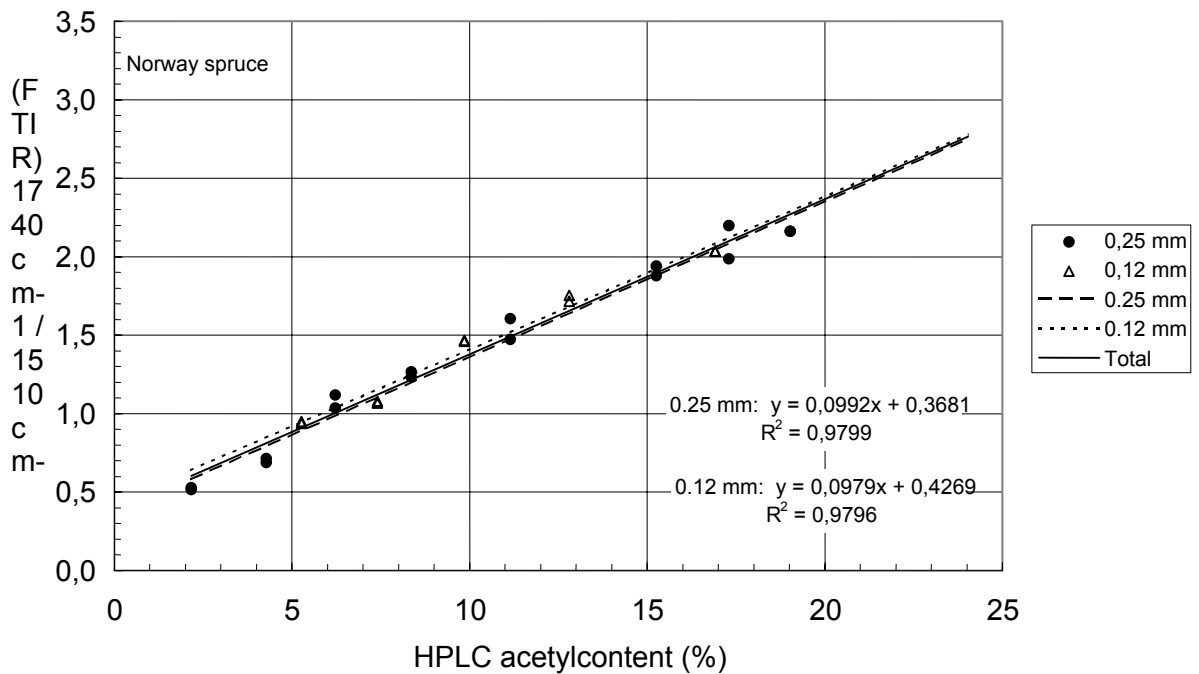


Figure 8: Correlation between FTIR and HPLC acetyl content of acetylated Norway spruce of various grinding sizes during sample preparation

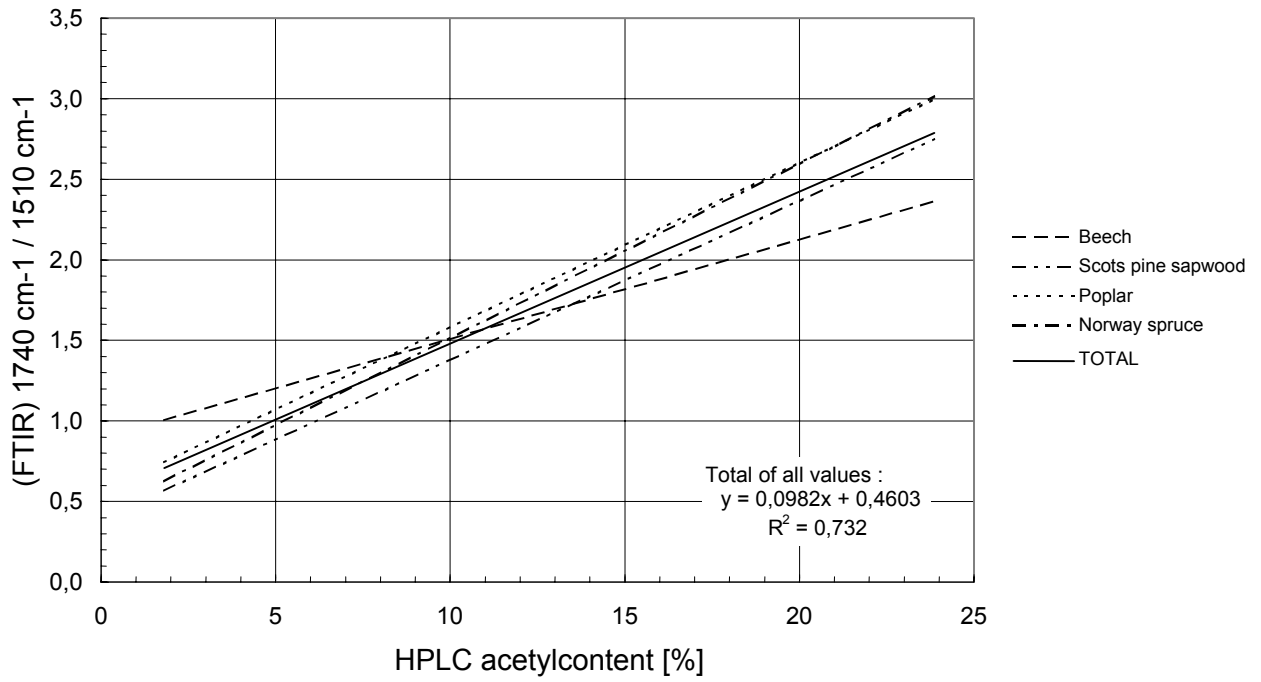


Figure 9: Correlation between FTIR peak ration of 1740 cm<sup>-1</sup> and 1510 cm<sup>-1</sup> and HPLC analysis of acetylated beech, Scots pine sapwood, poplar and Norway spruce

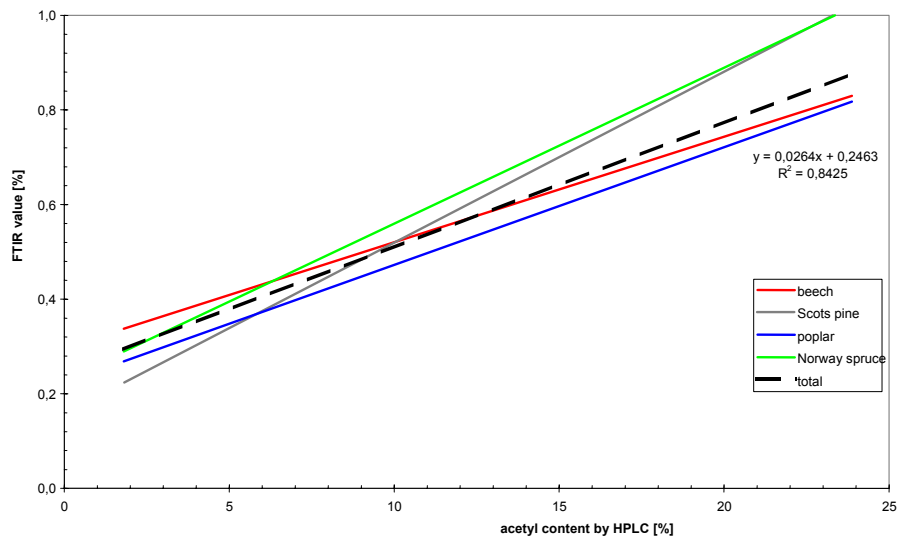


Figure 10: Correlation between FTIR peak ration of 1740 cm<sup>-1</sup> and 1060 cm<sup>-1</sup> and HPLC analysis of acetylated beech, Scots pine sapwood, poplar and Norway spruce

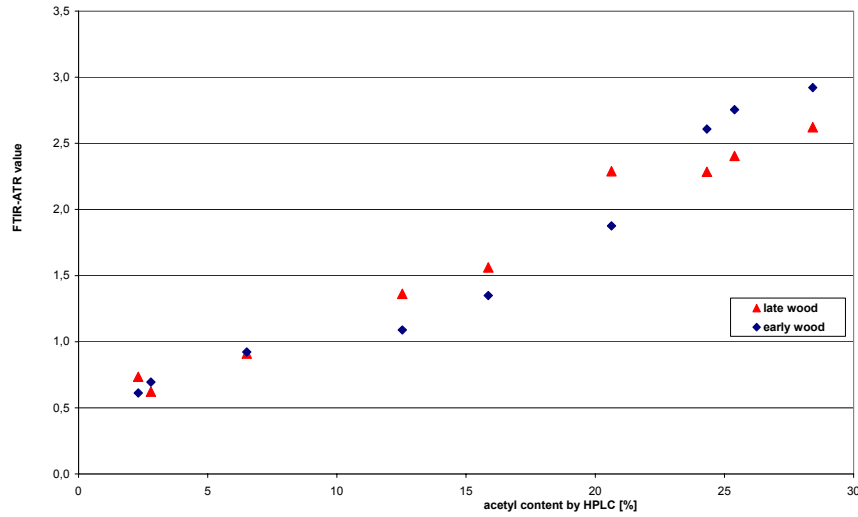


Figure 11: Initial comparison between FTIR-ATR analysis and HPLC acetyl content determinations of the transversal side of Scots pine sapwood. Each point represents a single value.

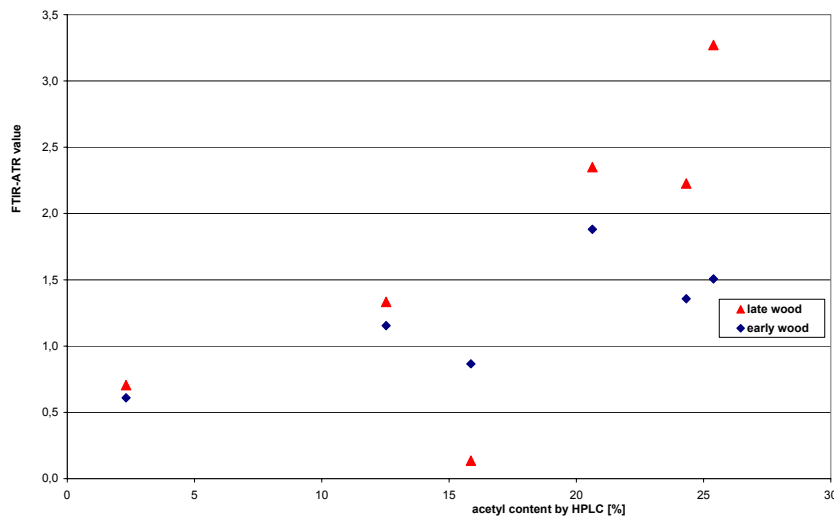


Figure 12: Initial comparison between FTIR-ATR analysis and HPLC acetyl content determinations of the cross cut side of Scots pine sapwood. Each point represents a single value..

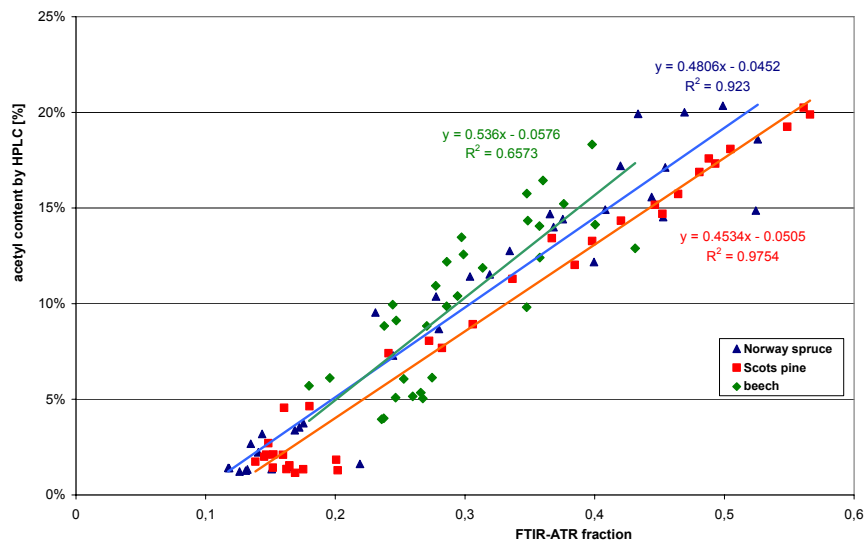


Figure 13: Correlation between FTIR-ATR analysis (ratio 1740/1010) and HPLC acetyl content determinations of Scots pine sapwood, Norway spruce and beech

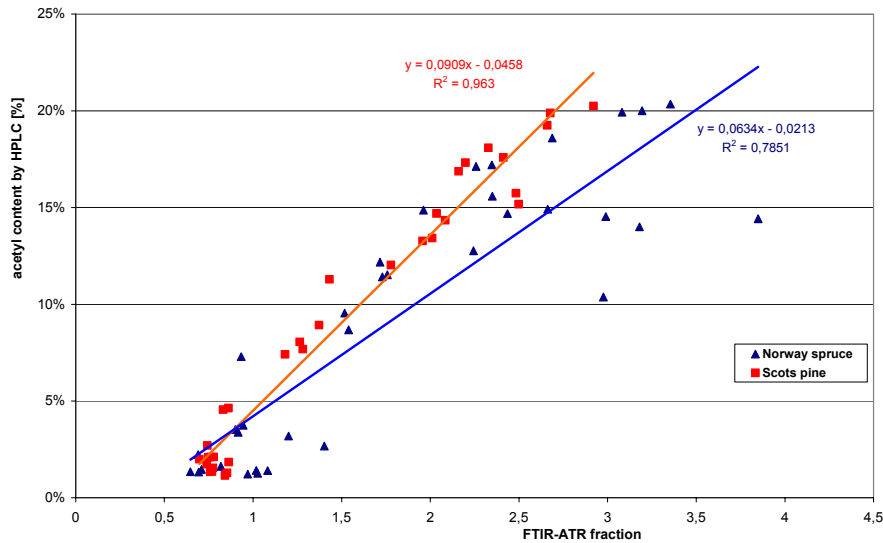


Figure 14: Correlation between FTIR-ATR analysis (ratio 1740/1510) and HPLC acetyl content determinations of Scots pine sapwood, Norway spruce and beech

### Autofluorescence

It is well known that lignin shows a specific absorption spectrum within the UV spectrum, and changes within the lignin structure result in a change in the spectrum obtained (Dawson *et al.* 1992, Frey-Wissling 1964, Fukazawa and Imagawa 1981, Goldschmid 1971, Pandey *et al.* 1998). This can be used for such things as the analysis of lignin degradation, or modification. The aromatic nature of the lignin determines its luminescence behaviour during excitation with UV-light. A part of the absorbed energy is emitted at a longer wavelength, an effect known as fluorescence. Polyphenols, such as lignin reveal a primary fluorescence (autofluorescence) within the blue spectrum when excited with UV-light. Recently, fluorescence spectroscopy has been used for determination of lignins originating from different wood species (Pandey *et al.* 1998, Billa *et al.* 1999). Hon and Shiraishi (1991) stated that cellulose contributes only to a small amount to the absorbance spectrum of wood tissue.

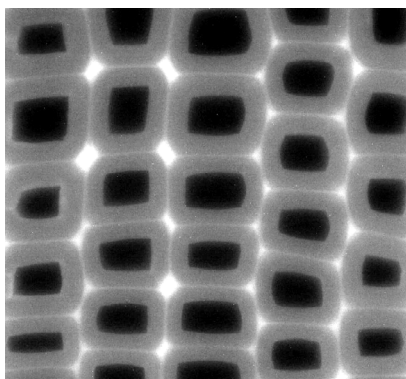
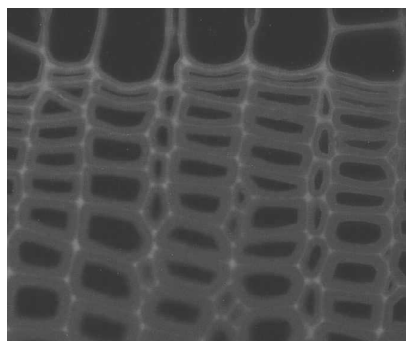
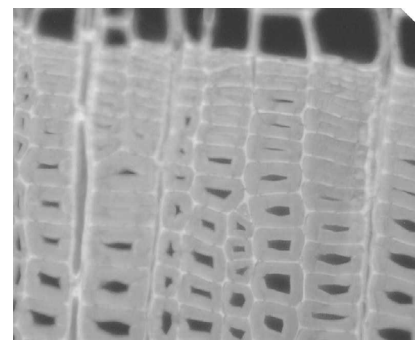


Figure 15: Fluorescence of lignin in Norway spruce. (100x oil immersion objective). Lignin rich cell corners and tracheid middle lamella reveal a strong fluorescence after irradiation with UV-light.



A



B

Figure 16: Fluorescence of lignin in Norway spruce xylem (latewood). A: untreated wood B: wood after acetylation to approx. 17% weight percent gain. Micrographs were taken with a objective.

The autofluorescence measured in this study undoubtedly originates from lignin. Microscopic images revealed stronger fluorescence in lignin rich structures such as the middle lamella and even more distinct in the cell corners (Fig. 15 and 16). Even at low degrees of acetylation - when



the carbohydrates were hardly acetylated - an effect on the fluorescence intensity was measured. Nevertheless contents of resin canals also showed some fluorescence. This was probably due to other phenolic or unsaturated aliphatic compounds with a conjugated  $\pi$ -electron system.

Our tests with sections mounted in glycerin could show a bathochromic shift of the fluorescence spectrum with increasing degree of acetylation, an effect that was not noticed in the analysis of wood blocks where the emission wavelength remained constant. The emitted wavelength after acetylation shifted from 500 nm to 550 nm for Scots pine sapwood and to 525 nm for beech. The intensity increased for both (Fig. 17, 18). According to Olmstead and Gray (1997) fluorescence characteristics of lignin is mainly determined by coniferyl alcohol and phenylcoumaran components. Both structures can more often be found in coniferous lignins than in angiosperm lignins. This might explain the lower correlation of the fluorescence intensity with acetylation degree in beech. The presence of other phenolic compounds must also be taken into consideration.

One major problem of interpreting fluorescence spectra is that they are not generally useful as a “fingerprinting technique” (Munck 1989). A common disadvantage of fluorescence spectroscopy and another possible source of disturbance is the fading of fluorescence with time. Fading is caused by photochemical degradation of the chromophores and will lead to an increasing loss of the fluorescence with prolonged irradiation. However, it is known that solvents and their pH, influence fluorescence too (Lakovicz 1983). Presence of phenolic wood extractives may also be a source of disturbance (Goldschmid 1971). Temperature, but also sample preparation may play a role as well (Kutscha and McOrmond 1972). Defects of the samples or uneven surfaces might cause fluctuation in absorption (Fukazawa and Imagawa 1981). Additional test results investigating these variables showed that this method is unsuitable for determining the acetylation level, since the measured change of autofluorescence of acetylated wood compared to untreated wood was mainly caused by reduction of the wood moisture content (and not the change in lignin).

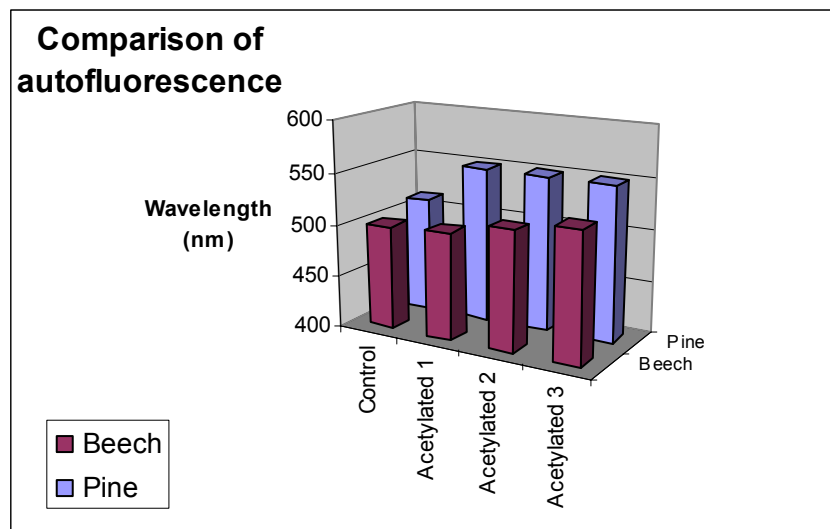


Figure 17: Correlation between autofluorescence and HPLC acetyl content of acetylated Scots pine ( $Ac_{max} = 23.4\%$ ) and beech ( $Ac_{max} = 19.4\%$ )

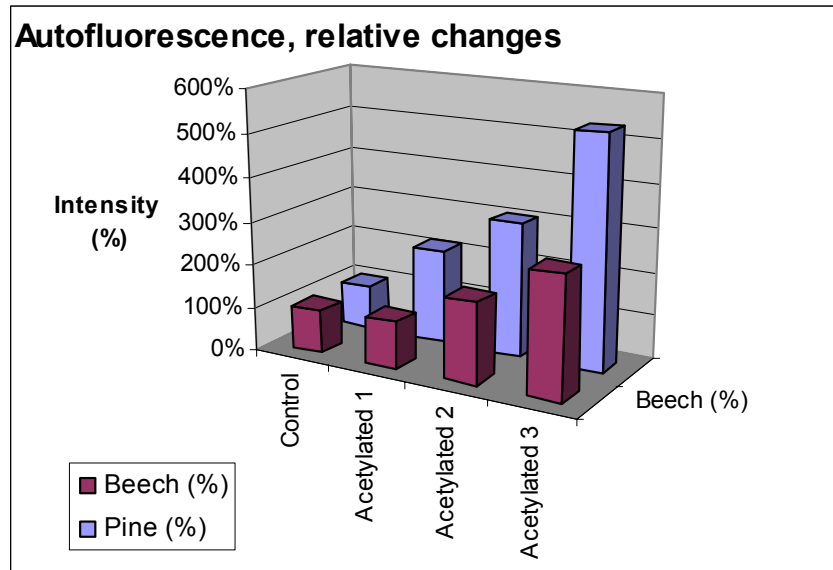


Figure 18: Correlation between relative changes in autofluorescence and HPLC acetyl content of acetylated Scots pine ( $Ac_{max} = 23.4\%$ ) and beech ( $Ac_{max} = 19.4\%$ )

**ToF-SIMS**

**Images**

In figure 19 ToF-SIMS images of the cross section of untreated and acetylated samples with different treatment levels are shown. A brighter colour represents a higher intensity of the measured negatively charged fragment  $CH_3CO_2$  (mass 59) and therefore a higher acetyl content. In order to enhance resolution, the intensity of fragment  $CH_3CO_2$  is divided by the total intensity (response of all fragments) for the image of the acetylated 4.6% WPG sample. The individual measurements are correlated to the fragment  $C_2H$ , which was found to be constant during all measurements.

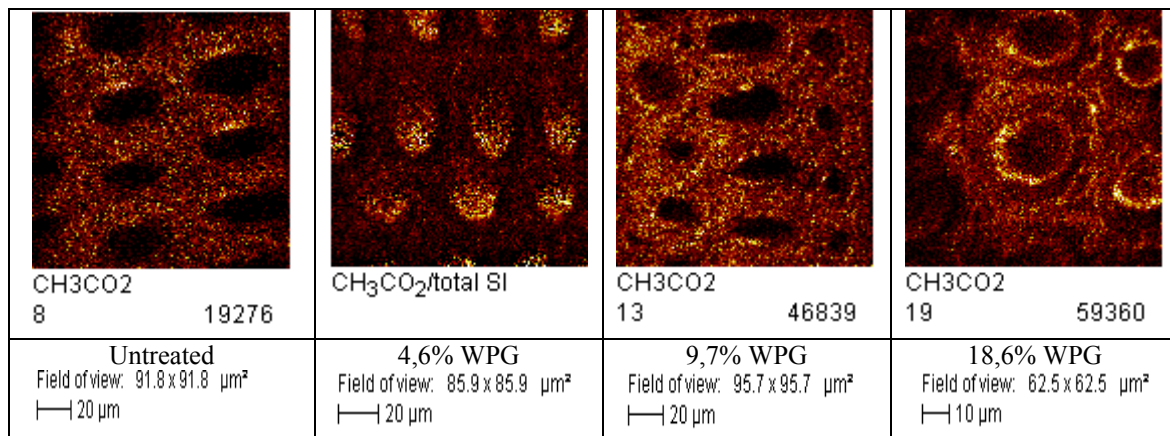


Figure 19. ToF-SIMS images for negative mass 59 ( $CH_3CO_2$ ) for untreated and acetylated Scots pine sapwood

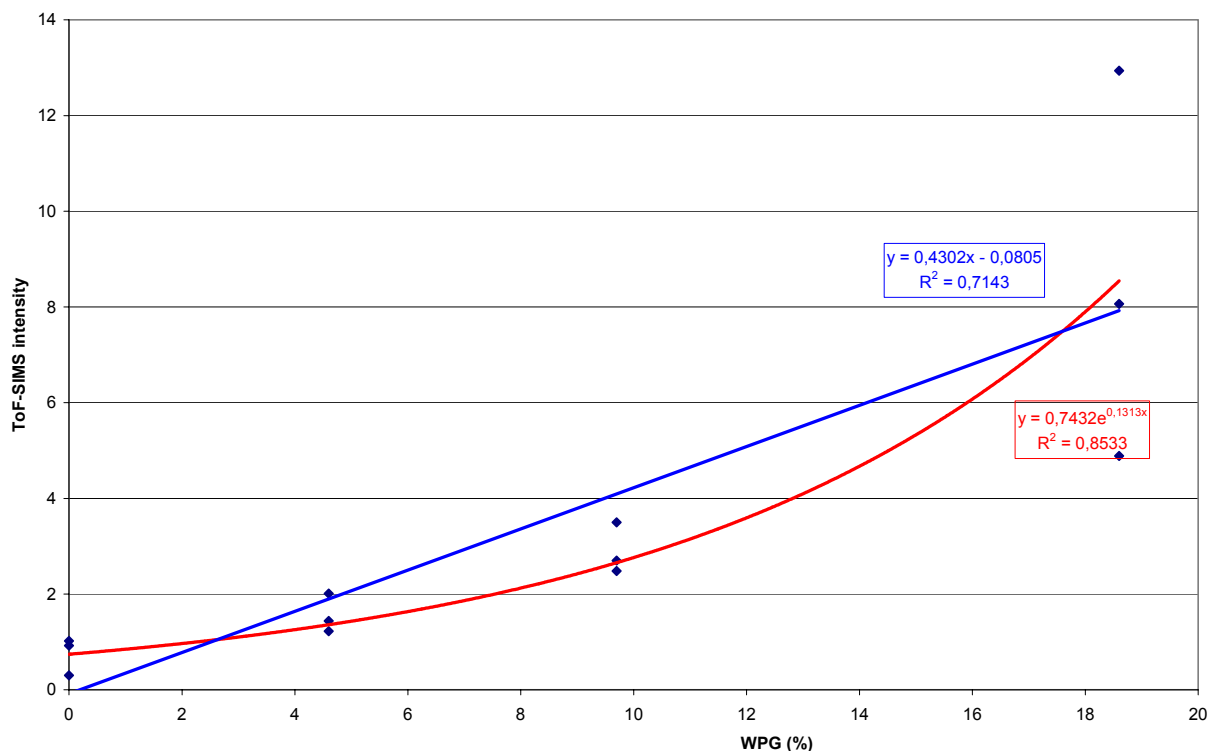
**WPG vs. ToF-SIMS intensity**

The best correlation between the acetylation level (WPG) and ToF-SIMS intensity was found for the negatively charged fragment  $CH_3CO_2$  (mass 59). Although an exponential regression better describes the findings, a linear regression is expected (Fig. 20). The sample of the highest WPG contained some silicon oil that is influencing the intensity measurements. ToF-SIMS seems to be

able to determine the acetylation content. However before usage of this analysis method, more testing needs to be done.

In general can be said that:

- the method looks repeatable on first sight, although sample preparation is critical.
- the measurements of the wood surface differs from spot to spot, due to inhomogeneity of the wood structure.
- besides measurement of the acetyl content the method could also be used for making images of the distribution of acetyl groups on a cellular level.
- samples need to be carefully prepared: the surface needs to be smooth and clean (without any interfering compounds like oils, waxes).
- ToF-SIMS is probably not suitable for quality control of industrial modified wood, since the required level of cleanliness can not be achieved on this scale.



**Figure 20: Relation between the acetylation level (Weight Percent Gain) and the ToF-SIMS Intensity for the negative mass 59.**

## CONCLUSIONS

For quality control it is necessary to determine the treatment level of a modification technique. This can either be a direct method (for example chemical analysis) or an indirect method where a changed wood property is used to determine the treatment level (e.g. equilibrium moisture content). This latter method though is usually very time consuming and will take at least several days to perform. A *quantitative* analytical method is needed which directly shows the degree of acetylation. Table 2 shows the suitability of the various analytical methods for this purpose.

**Table 2: Suitability of various analytical methods to determine the degree of acetylation of acetylated wood for quality control on a commercial level**

	WPG	Titration	HPLC	GC	FTIR-KBr	FTIR-ATR	Autofluorescence	ToF-SIMS
Ease of sample preparation	+	--	--	--	-	+	--	-
Costs of required equipment	++	+	-	-	-	-	-	--
Labour intensity	+	--	--	--	-	+	--	-
Distinction between untreated and acetylated wood	+	+	+	+	+	+	--	+
Determination of degree of acetylation	+	+	++	++	-	--	-----	?
Suitability for solid wood in large dimensions	--	+	+	+	+	+		+

*Titration = non selective.*

The main advantage of the HPLC-method is the high accuracy in determining the acetyl content, but is rather labour intensive and time consuming. Titration seems to give quite similar results, is a little less time consuming, but nevertheless still quite labour intensive. Another disadvantage of titration compared to HPLC is that it does not make any difference between various acids analysed.

Actually, all techniques, apart from the FTIR-ATR are still time consuming and labour intensive. For a rough indication of the degree of acetylation it is possible to use this relatively fast method. It could be used to check whether timber is acetylated. When the actual degree of acetylation is required, one of the more labour intensive and time consuming, but more accurate analytical techniques should be used.

Within a few years acetylated solid wood will probably be commercially available. This material will not differ much from untreated wood as far as appearance is concerned. A relatively fast method is therefore required which at least should reveal whether or not a piece of wood is acetylated. This method should give a result within minutes comparable to the colouring agents used to indicate preservative treated timber. Goldstein *et al.* (1961) used a colouring agent which indicated acetyl groups and could even give a rough indication of the degree of acetylation depending on the colour which varied from yellow to purple to green. The company which sold this chemical (Cyanamid) has been split up though and all brochures and recipes are thrown away because these products have not been sold for more than 15 years. Similar comments were made by other companies that were involved in that particular part of research on analysing acetylated solid wood. Several attempts have been made since then in co-operation with suppliers of indicators to find a colouring agent and method which is specific for acetyl groups or ester bonds, all of them without any result. Further attempts in that area will be continued.

## ACKNOWLEDGEMENTS

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## The Kinetics of Acetylation Reactions

Callum A.S. Hill

School of Agricultural and Forest Sciences, University of Wales Bangor, Deiniol Road, Bangor, Gwynedd, LL57 2UW, UK

**Keywords:** Acetylation, anhydride, kinetics, diffusion

### ABSTRACT

The results of extensive studies into the kinetics of the reaction of linear chain anhydrides with solid wood samples and the modelling of these reactions within the wood cell wall are presented. Studies indicate that for reaction with acetic anhydride, the kinetics is diffusion limited throughout, whereas with longer chain anhydrides the initial reaction is reaction limited, with diffusion dominating thereafter. The results have implications regarding the distribution of adduct within the cell wall and the extent of reaction of the reagents with the cell wall polymeric components. Where the reaction is diffusion limited, the relative rates of reaction with the different cell wall hydroxyl environments is unimportant. Conversely, where the reaction is reaction limited, the relative rates of reaction with the different hydroxyl environments assumes greater importance.

### INTRODUCTION

The reaction of any reagent with a complex substrate such as wood is inherently complicated. Chemically, the hydroxyl groups can be distinguished as being phenolic, benzylic, or alcoholic on the lignin regions, and alcoholic in the carbohydrate. The alcoholic hydroxyl's may be either primary or secondary, the phenolic hydroxyl's are attached to an aromatic ring which has various substituents attached. Thus, each of these groups will exhibit a different reactivity towards anhydride reagents. For example it has been demonstrated that the primary hydroxyls of cellulose in cotton linters are more reactive to acetylation.

The immediate stereochemical environment surrounding a reacting OH group will also affect the reaction kinetics, which is of particular importance when the reaction is performed in a solid substrate.

In addition, the reaction of acetic anhydride with wood generates acetic acid (HOAc) as a by-product. At low concentrations up to *ca.* 10% HOAc in the anhydride, it has been observed that the reaction is accelerated, but at higher concentrations a retardation occurs.

The wood ultrastructure is a major factor, since the reagent molecules have to diffuse through the wood matrix to reach the reactive sites. Thus apart from in the initial stages, the reaction will be expected to be dominated by diffusion processes.

The hydroxyl groups of the cell wall polymers form extensive hydrogen bonding networks within the matrix, and reaction of a reagent with an OH group requires the breaking of an H-bond. If the breaking of hydrogen bonds is a slow process compared with the reaction of the anhydride with the OH group, then this will be the determining factor in the kinetics.



In the simplest possible analysis, a reaction with wood can be considered to be dominated by two processes, surface and bulk effects. The former is associated with reaction at or near the surface of the substrate and is assigned to the domination of the reaction kinetics by chemical reaction process. As the reaction proceeds, the bulk reactions assume increasing importance, and the kinetics will therefore be expected to be influenced more by diffusion dominated processes. Whether diffusion kinetics are indeed observed will depend critically upon the relative rates of diffusion and reaction, if the former is the slower process, then the reaction will be diffusion limited, but if the latter is slower then an alternative kinetic process will be observed.

### ***Surface reaction processes***

If it is assumed that during the initial stages of the process that the reaction sites are located at or near the wood surface, then diffusion can be neglected and the rate of reaction will be dependent upon the concentration of the anhydride molecules ( $[anhyd]$ ) and the wood cell wall polymer hydroxyl groups ( $[OH]$ ), and the rate constant of reaction ( $k$ ). A rate expression for this reaction can be written:

$$\text{Rate} = d[OH]/dt = -k [OH][anhyd] \quad (1)$$

This is a conventional second-order rate equation. If it is further assumed that during the initial stages of the reaction the anhydride reagent is present in a large excess, then the rate becomes dependent upon the concentration of the hydroxyl groups only:

$$\text{Rate} = d[OH]/dt = -k' [OH] \quad (2)$$

The assumption that the concentration of anhydride does not vary during the reaction is valid in situations where there is a very large reservoir of anhydride molecules. Equation 2 is a pseudo first-order rate expression, with  $k'$  being the related rate constant. Such an expression can be rearranged and integrated to yield the following expression:

$$\ln([OH]_t/[OH]_0) = -k't \quad (3)$$

Where  $[OH]_t$  is the concentration of OH groups remaining *unreacted* at time  $t$ , and  $[OH]_0$  the concentration of OH groups at time zero. Thus, it is possible to determine the pseudo first-order rate constant by plotting the natural logarithm of  $[OH]_t/[OH]_0$  against time, which yields a straight line of slope  $-k'$  if first-order kinetics is obeyed.

### ***Bulk reaction processes***

As the reaction proceeds, the diffusion of the reagent into the wood matrix assumes greater importance, and in the situation where the chemical reaction is rapid, compared with diffusion rate, the reaction will be under diffusion control. Where a process is under diffusion control, the mass change of a sample due to diffusion of molecules into the sample obeys the following relationship:

$$m = a.t^{1/2} \quad (4)$$

Where  $a$  is a constant related to the rate of diffusion. Thus a plot of the mass gain against square root time will give a linear relationship of gradient  $a$ .

### ***Pyridine catalysed anhydride modifications***

It is well known that the reaction of wood with anhydride reagents larger than acetic anhydride is a slow process, and may not occur at all unless the wood is in a pre-swollen state. For the

studies reported, pyridine was used as a reaction solvent since it swells the wood cell wall and allows for reaction with larger anhydride reagents to take place at an acceptable rate. These studies are to promote a better understanding of the wood-anhydride reaction process, and there is no suggestion that pyridine would ever be acceptable in an industrial process. It is also known that pyridine catalyses the reaction, and thus the studies reported here may not be directly applicable to situations where the reaction does not take place in a swollen cell wall in the presence of a catalyst.

## EXPERIMENTAL

### *Kinetics studies*

Corsican pine (*Pinus nigra*) sapwood was selected for these studies. Sample sizes of 20 mm x 20 mm x 5mm (Radial x tangential x longitudinal) were cut from kiln dried wood, extracted using a mixture of toluene : methanol : acetone (4 : 1 : 1, by volume) for six hours, and dried in an oven overnight (105°C) before use. A weight loss of 3% was recorded due to such treatment. For modification with the pyridine/ anhydride system, the following method was adopted (Hill and Jones 1996). Pre-weighed samples (five replicates) were vacuum impregnated with water free pyridine using a rotary vacuum pump, then added to a round bottom flask containing 100ml of pyridine set in an oil bath regulated to the desired temperature. An hour was allowed for the samples to achieve the required temperature, then sufficient anhydride (pre-heated to the required temperature) to make a one molar solution was added. At the termination of the reaction, the pyridine solution was decanted off and the blocks added to acetone at room temperature to quench the reaction. The blocks were left to stand in the acetone for one hour, then transferred to a Soxhlet apparatus, extracted as previously and dried in an oven at 105°C overnight. Such a treatment was found to be adequate to ensure that all traces of solvent, reactant and by-product were removed (Hill and Jones, 1996; Hill *et al.*, 1998).

### *Impregnation studies*

In a further set of experiments, extractive-free samples of Corsican pine sapwood were impregnated with either 100% acetic anhydride or 95% acetic anhydride with 5% pyridine at room temperature. These samples were then added to a flask containing either the neat anhydride, or the 5% pyridine/anhydride mix, at a temperature of 100°C. Samples were added at different time intervals, then at the end of the reaction period the hot reagent was decanted off and ice-cold acetone added to the flask to quench the reaction. Samples were extracted and dried in the usual way (Hill *et al.*, 2000)

## RESULTS

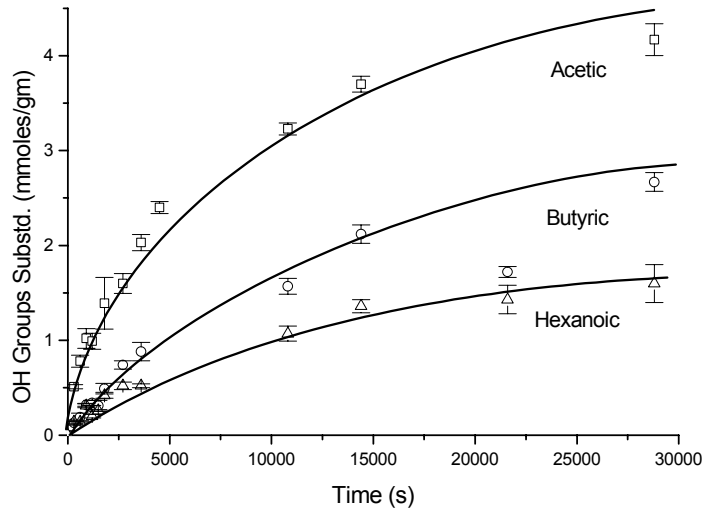
### *Reaction profiles*

A typical set of reaction profiles for the reaction of acetic, butyric and hexanoic anhydride with wood samples at 100°C is shown in Fig. 1. The data shows that the smaller the size of anhydride, the more rapid the rate of substitution of OH groups in the wood. After 8 hours reaction time, levels of substitution of *ca.* 4, 2.2 and 1.4 millimoles of OH groups per gram of oven-dry wood are observed for acetic, butyric and hexanoic anhydrides respectively.

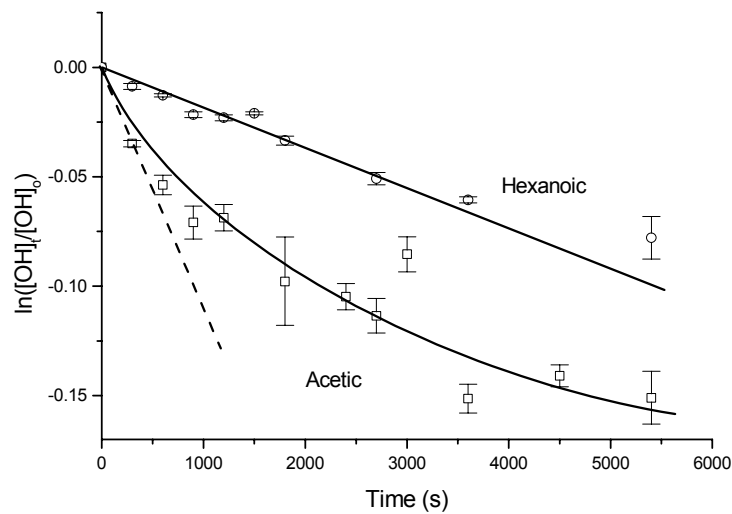
Analysis of the same data for acetic and hexanoic anhydrides in terms of first order kinetics is shown in Fig. 2. With hexanoic anhydride, the data points exhibit a good linear relationship up to about 4000 seconds reaction time, but no such relationship is seen with the data for acetic anhydride. In the extensive studies performed at Bangor, it has been found that such plots show linear relationships for more extended periods after the initiation of reaction as:

1. the size of anhydride increases, and
2. as the temperature of reaction is decreased

The implications of this will be discussed later.



**Figure 1: Reaction profiles for acetic, butyric and hexanoic anhydrides**



**Figure 2: First order kinetics plot for acetic and hexanoic anhydride**

When the same data is analysed in terms of diffusion, the plot in Fig. 3 is obtained. An essentially linear relationship of the data is obtained for acetic anhydride up to reaction times of  $10^4$  seconds, whereas both butyric and hexanoic anhydrides exhibit sigmoidal relationships of the data points.

The effect of temperature of reaction upon the diffusion reaction profiles is shown for propionic anhydride at reaction temperatures of 60, 90 and 120°C in Fig. 4.

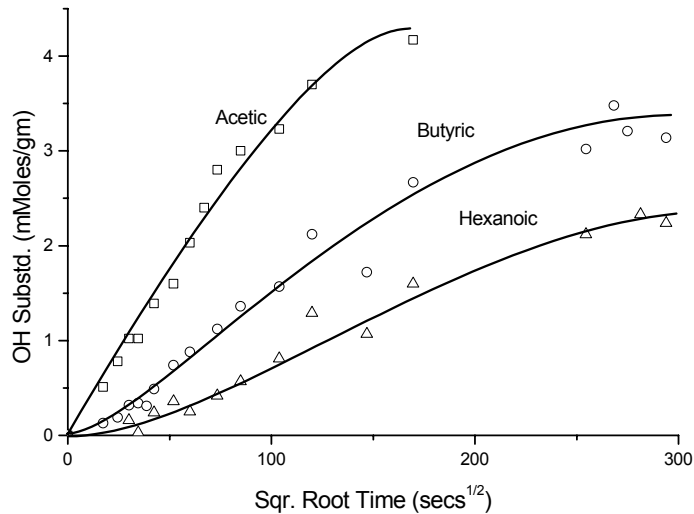


Figure 3: Diffusion kinetics plot for acetic, butyric and hexanoic anhydrides

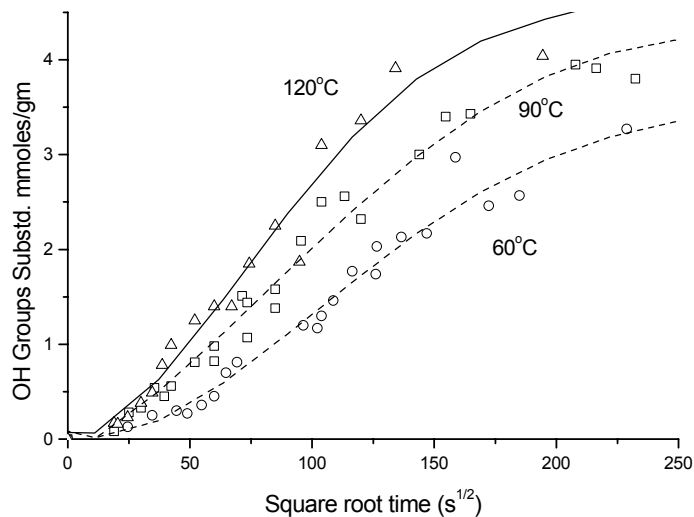


Figure 4: Diffusion kinetics plot for propionic anhydride at different temperatures

All of the reactions at the three temperatures show sigmoidal relationships, but as the temperature of reaction is reduced, the 'induction period' of the profiles extends for greater periods of time.

#### **Modelling the reaction process**

In order to model the reaction process taking place within the cell wall of wood, a programme was developed to run on a PC which was based upon percolation theory (Hill and Hillier, 1998; 1999). The programme consisted of two elements:

1. A network within which 'molecules' could diffuse and react
2. A means of varying the rate of reaction of the 'molecules' at reactive sites in the network

#### **The network**

A network was generated upon a square two dimensional lattice. This was achieved by populating initially empty sites on the lattice. The extent of population of the site was controlled by setting a parameter ' $p$ ' (called the filling parameter). Thus if  $p$  was 0.1, the sites were randomly populated such that 10% of the possible sites were filled, if the parameter  $p$  was set at 0.8, then 80% of the sites were randomly populated, etc. An example of such a network

generated for a  $p$  value of 0.8 is shown in Fig. 5. These sites were then deemed to be connected if they were adjacent to one another either horizontally, or vertically.

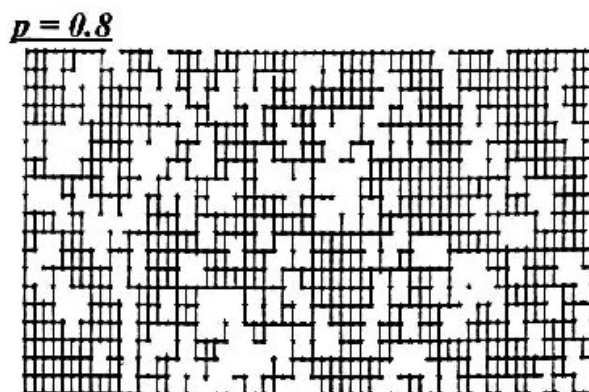


Figure 5: Example network generated with an 80% filling parameter

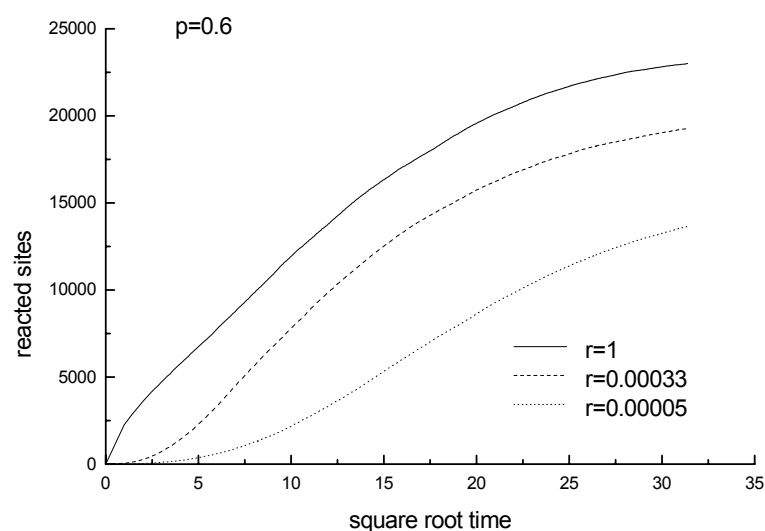


Figure 6: Diffusion plots generated on a network with a filling parameter of 60% and with reaction probabilities as indicated

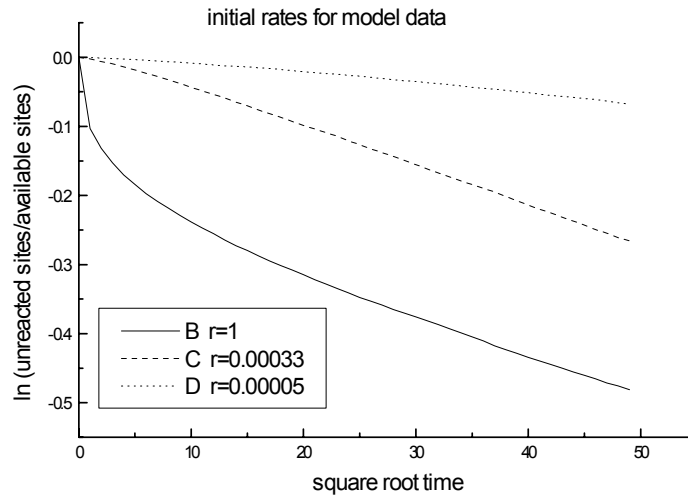
### Reaction and diffusion upon the networks

The sites on the top of the network were filled with molecules and were allowed to move either horizontally or vertically. If a molecule moved upwards off the network, then this site was filled at the next computing step. The probability of reaction of a molecule with a site on the network was set by a further parameter ' $r$ ' (called the reaction probability). Reactions were then run for different values of  $p$  and  $r$ . It was found that results which best fitted the experimental data were obtained for a network set at a filling parameter of  $p=0.6$ , with various values of  $r$ . An example of a diffusion plot with  $r=1$ ,  $3.3 \times 10^{-4}$  and  $5 \times 10^{-5}$  is shown in Fig. 6. The same data is shown in a first order kinetic plot in Fig. 7.

These plots show that the observed first order and diffusion kinetic profiles can be replicated simply by varying the value of the reaction parameter ( $r$ ). Thus, when  $r$  is set at a value of 1, a molecule will diffuse to a site and react immediately at that site (provided that the site has not already been substituted). Such a reaction is diffusion limited and shows a linear reaction profile when plotted in terms of diffusion, but a non-linear profile when analysed as a first order kinetics

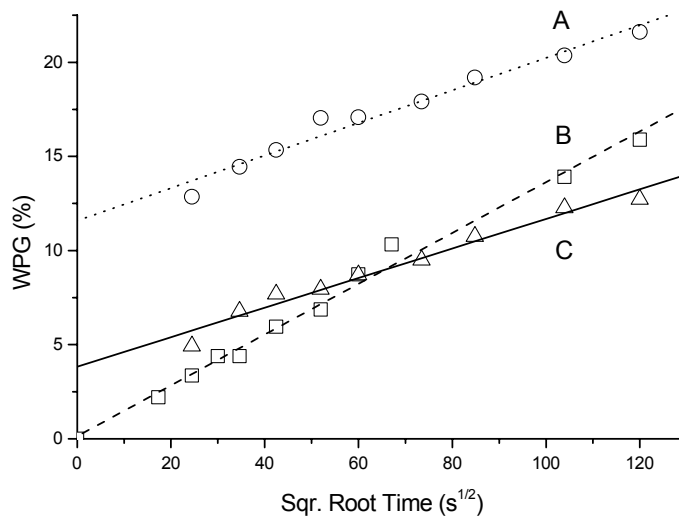
plot. The departure from linearity of the diffusion profile at longer reaction times is due to there being relatively few unreacted sites available.

As the value of  $r$  is decreased, the diffusion reaction profiles show increasingly longer induction periods. The values of  $r$  chosen in these cases indicate that an individual molecule would visit in the order of 10,000 or 100,000 sites before reacting.



**Figure 7:** First order plots for simulation on a network with a filling parameter of 60% and with reaction probabilities as indicated

**Pre-impregnation of samples**



**Figure 8:** Diffusion reaction profiles for wood samples pre-impregnated with 95% acetic anhydride and 5% pyridine (A), 10% acetic anhydride and 90% pyridine (C), and for reaction with 10% acetic anhydride and 90% pyridine (no pre-impregnation) (B).

Although the above studies are of academic interest, the reaction methods would not be suitable for use in an industrial process, therefore the effect of impregnating the wood samples with anhydride upon the kinetic profiles were also investigated. The results of this study are shown in Fig. 8. With plot A (impregnation with a mixture of 95% acetic anhydride and 5% pyridine), a very rapid reaction takes place initially, then the reaction becomes diffusion limited. With plot C (impregnation with 100% acetic anhydride), a rapid reaction also takes place initially, followed by a diffusion limited reaction, but the reaction rate and rate of diffusion are both lower than in plot A. Plot B shows the reaction profile for a reaction using pre-heated pyridine impregnated samples to which are added a solution of 10% acetic anhydride and 90% pyridine. In plot B, the reaction is diffusion limited throughout, with no initially rapid reaction, but the rate of diffusion is much faster than in plot A or C.

## DISCUSSION

The model has shown that it is necessary to consider both the rate of reaction of anhydride molecules with the cell wall OH groups and the rate of diffusion of these molecules within the cell wall. In the case of acetic anhydride under the conditions studied in these experiments, the reaction is diffusion controlled. That means that the rate determining step of the reaction depends only upon the time it takes for an anhydride molecule to reach a reactive site, but once a molecule has arrived it will react with a high probability. The implication of this observation is that any differences in the reactivity of different OH environments are of little importance. Thus the distribution of substituted OH sites will be controlled only by diffusion, and a reaction front will occur with the distribution of reacted sites spreading out from the lumen surface.

For larger anhydrides, the reaction probability at a particular OH site is much lower. The model indicates that an anhydride molecule will 'visit' many sites before reaction occurs. Therefore the rate of reaction with specific OH sites assumes greater importance in this case and the distribution of reacted OH sites will be more diffuse across the cell wall.

The 'induction time' observed in diffusion plots of the kinetics is due to the kinetics being reaction limited rather than diffusion limited in the initial stages of the reaction process. With the diffusion plot for the reaction of propionic anhydride, it can be seen that this induction period occurs for shorter times as the reaction temperature is increased. This indicates that diffusion limited kinetics become dominant earlier in the reaction process. Thus, the temperature of the reaction would also be expected to affect the distribution of substitution throughout the cell wall, with a more diffuse distribution of substitution observed as the reaction temperature is decreased.

All of the above reactions were performed under conditions where the reagent is not present in the cell wall before reaction is initiated. Impregnation of the wood with reagent, or reagent/catalyst results in a very rapid initial reaction. This is because the cell wall already contains reagent when the reaction starts. Once this reagent has been 'used up', the reaction then becomes diffusion limited, as further reagent now has to diffuse to reactive sites in the cell wall. The presence of pyridine, even at a concentration of only 5%, has a dramatic effect upon the rate of reaction, although a lesser effect upon the rate of diffusion. The impregnation of the cell wall with reagent prior to reaction would undoubtedly affect the distribution of reacted sites within the cell wall, with a more even distribution of reaction occurring.

## CONCLUSIONS

Reaction conditions (temperature, time, concentration of reagent, presence of catalyst, whether the wood was impregnated with reagent prior to initiation of reaction) have a very significant influence upon the reaction kinetic, and therefore upon the distribution of reacted sites within the cell wall. Thus when measuring the properties of modified wood (decay resistance, dimensional stability etc.), it is very important that all of the reaction conditions are controlled precisely. Furthermore, any differences in reaction conditions may result in such properties being different. This should always be borne in mind when comparing results in the literature.

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## Preliminary Research on the Biological Resistance of Thermally Modified Wood

B. Mazela, R. Zakrzewski, W. Grześkowiak, G. Cofta, M. Bartkowiak

Agricultural University of Poznań, Institute of Chemical Wood Technology, 38/42 Wojska Polskiego st., 60-637 Poznań, Poland, e-mail: bartsimp@owl.au.poznan.pl

**Keywords:** pine wood, thermal and hydrothermal treatment, biological resistance, fungal degradation, mycological test EN-113.

### ABSTRACT

Sapwood of Scots pine (*Pinus sylvestris* L.), was subjected to thermal and hydrothermal treatment and the biological resistance of this material to wood destroying fungi determined. Wood was modified in an atmosphere of air, or water vapour at the following temperatures: 160, 190 and 220°C for 6, or 24 hours. Biological resistance of modified wood was determined by applying an accelerated mycological test conducted according to procedures contained in the EN 113 standard. The following test fungi were used in the experiment: *Coniophora puteana*, *Gleophyllum trabeum*, *Poria placenta* and *Coriolus versicolor*. The results showed a correlation between the conditions of the hydrothermal process of wood treatment and biological resistance of the treated wood to test fungi. Wood modified in an atmosphere of water vapour at a temperature of 220°C for 24 hours showed the highest resistance against the selected organisms.

### INTRODUCTION

Wood, as a biopolymer composite, has been known and recognised as a construction material for a long time. However, considerable possibilities still remain associated with the improvement of wood natural quality characteristics such as dimensional stability, or resistance to biodegradation, which might prolong the service life of wood products. In order to achieve these objectives, wood modification has been developed as a method of equipping this material with new properties. Both wood physico-chemical characteristics and service properties depend on its chemical composition; first and foremost, on the presence of hydrophilic carbohydrate constituents and their structure in cell walls. Increased resistance to the activity of biotic and abiotic agents, as well as improvement of dimensional stability of wood, can be achieved by the introduction of chemical compounds, which will either block the hydroxyl groups or exhibit toxicity to wood decomposing organisms. However, both types of these compounds may pose a serious threat to the environment once the wood elements, which had been treated with such chemicals, are no longer necessary. Reduced wood hygroscopicity as a result of a reduced number of hydroxyl groups should have a positive influence on wood service properties. Hydroxyl groups in carbohydrate wood constituents (cellulose and hemicelluloses) are reduced by heat application, but it is important to remember that its upper temperature limit should not exceed the point at which active pyrolysis begins (260°C). Results of experiments carried out by Madorsky (1964) as well as by Shafizadeh and Bradbury (1979) revealed that, at temperatures below 250°C, cellulose decomposition proceeded at a low rate with the production of H<sub>2</sub>O, CO and CO<sub>2</sub>, indicating that processes of dehydration and decarboxylation were taking place. In addition, in these conditions, the degree of cellulose polymerisation is reduced considerably but its reduction does not result in weight loss (Broido *et al.* 1976). Basch and Lewin (1973a, b, 1974) reported an increase in the extent of cellulose crystallinity heated in vacuum conditions at the temperature of 200°C. At temperatures below 200°C, non-cellulosic carbohydrates, mono-

and oligosaccharides and polysaccharides polymerise, forming dextrans and branched polysaccharides. This process is accompanied, as in the case of cellulose, by liberation of H<sub>2</sub>O, CO and CO<sub>2</sub>. Lignin, which is considered as the most thermo-resistant wood constituent, undergoes slight decomposition at temperatures below 200°C (Ramiach 1970). Hatekeyama (1969) demonstrated that lignin undergoes softening at the temperature range of 100-180°C.

The above-mentioned processes served as a basis for the development, in the final years of the previous century, of a new method of wood modification by way of its multi-variant thermal treatment (Boonstra *et al.* 1998, Jamsa and Viitaniemi 1998, Garrote *et al.* 1999, Rapp *et al.* 2000, Syrjanen *et al.* 2000). Experiments on the biological resistance of thermally modified wood were also undertaken at the Institute of Chemical Wood Technology of Poznań Agricultural University. The objective of those investigations was to determine the impact of conditions of this process on wood resistance against white and brown rot fungal decomposition.

## METHODOLOGY

### **Wood**

Sapwood samples of Scots pine (*Pinus sylvestris* L.) measuring 50 x 15 x 5 mm (the last measurement longitudinally) were used in the investigations. Samples were conditioned for approximately 2 weeks. Mean wood absolute moisture content determined on a series of representative samples was about 12%, while the mean density determined at the above moisture content amounted to about 0.570 g/cm<sup>3</sup>.

### **Thermal treatment**

Samples were placed on perforated shelves, which were fixed in a tight metal container equipped with connector pipes, which allowed for the introduction of water vapour into it and disposal of the steam-gaseous products of decomposition. The container was placed in a chamber furnace equipped with a control system, allowing programming of the rate and time of heating. Thermal modification was carried out in the atmosphere of air and water vapour. The purpose of the application of water vapour was to remove products of hemicellulose hydrolysis from wood and, in so doing, depriving the wood of products readily available for fungi. Experiments carried out in an air atmosphere consisted of heating the container to a temperature of 110°C in 20 minutes and maintaining this temperature for 2 hours. Next, in a period of 60 minutes, the temperature inside the container was increased to the required treatment temperature (160, 190 and 220°C). Treatment time was 6, or 24 hours. For heating in the atmosphere of water vapour, no intermediate treatment stage at the temperature of 110°C was applied. The container chamber was brought to the above-mentioned temperature levels for treatment times of 6, or 24 hours.

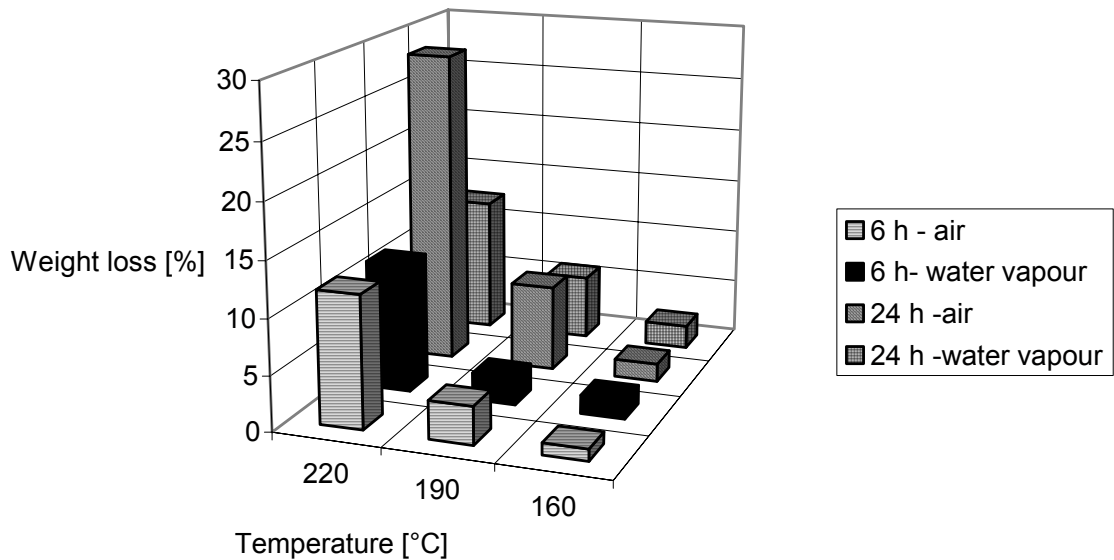
### **Biological investigations**

After thermal treatment, the wood was subjected to investigations to determine its resistance against selected species of fungi characteristic for white and brown rot. Mycological tests were carried out applying a rapid method based on recommendations found in the EN 113 standard. Eight samples were used for each test, five samples were used to calculate weight losses caused by the test fungi and three to calculate correction coefficients. The period of the exposure to fungal action was 8 weeks. The following four fungal species were used in the experiments: *Coniophora puteana* (Schum. ex. Fr.) Karst. strain BAM, Ebw. 15; *Coriolus versicolor* (L. ex Fr.) Quel. strain BAM Ebw. 214; *Gleophyllum trabeum* (Persoon ex Fries) Murrill strain BAM Ebw. 109; *Poria placenta* (Fr.) Cke. strain BAM Ebw 125.

## RESULTS

### *Thermal treatment*

The thermal wood treatment caused weight losses of samples, which increased with the increase of temperature and time of treatment, as presented in Figure 1. Weight losses after 6 hours thermal treatment in air and water vapour atmospheres were comparable and increased from about 2% at a temperature of 160°C, to about 12% at a temperature of 220°C. The rate of the sample weight loss for wood subjected to treatment for 24 hours was considerably greater in the air atmosphere, with weight losses increasing respectively from 2% to over 28%, in comparison with samples subjected to the action of water vapour for which weight losses amounted to: 2.1% at a temperature of 160°C, 5.9% at 190°C and 12.4% at 220°C. With the increase of sample weight losses, an increasing darkening of wood was observed.



*Figure 1. Mean weight loss of wood modified thermally in air and water vapour*

### *Activity of test fungi*

The measure of the activity of test fungi and, consequently, the indicator of the effectiveness of the performed investigations, was the weight loss of control samples (Table 1). The performed experiments showed high activity of brown rot fungi, as weight losses of controls, attributed to their activity, ranged in the interval of 23 to 46%. These values exceeded values of weight losses of control samples for individual fungi as minimal values required in the EN 113 standard. *C. versicolor* fungus was found to show lower activity against natural wood, because this species of fungus does not specialise in the decomposition of coniferous wood species. Weight losses at the level of only 15% could be attributed to the adjustment of this organism from the decomposition of wood of broad-leaved species.

### *Wood moisture content*

After mycological tests, wood reached moisture contents considerably exceeding the fibre saturation point for all of the mycological tests (Table 1). These values confirm the advantageous conditions for the decomposition of modified wood in which these experiments were carried out.

**Table 1: Wood weight losses (WL, %) and wood moisture content (MC, %) due to the action of test fungi in an agar-block test for control samples.**

Process parameters	<i>Coniophora puteana</i>		<i>Gleophyllum trabeum</i>		<i>Poria placenta</i>		<i>Coriolus versicolor</i>	
	WL	MC	WL	MC	WL	MC	WL	MC
Test control samples	39.4	81.0	23.5	100.4	45.8	53.6	15.4	69.6

### **Biological resistance of wood modified at the temperature of 160°C for the period of 6 hours**

The observed resistance of these experimental samples against the activity of test fungi was very low (Table 2). In the case of *P. placenta* and *C. versicolor* fungi, mean weight losses of modified samples were similar to those recorded in the case of weight losses of control samples. Samples of wood modified in an air atmosphere and subjected to the activity of *C. puteana* and *G. trabeum* fungi exhibited weight losses about 5% higher than those observed in the case of control samples. Moisture content in samples examined after the mycological test ranged from 75 to 140%, depending on the species of the tested fungus.

### **Biological resistance of wood modified at the temperature of 160°C for the period of 24 hours**

Following thermal treatment in the atmosphere of air, only samples subjected to the action of *C. puteana* fungus exhibited an increased biological resistance (Table 2). Weight losses of the examined samples caused by the activity of this fungus amounted to about 9%, while the weight loss of control samples reached almost 40%. No improvement of wood biological properties was observed for the remaining variants within the examined technological parameters of thermal treatment. Moisture content of thermally modified wood, after the exposure to the action of test fungi, ranged from 45 to 104%.

**Table 2: List of wood weight losses in the result of action of test fungi (WL, %) and wood moisture content (MC, %) in an agar-block test**

Process parameters	<i>Coniophora puteana</i>		<i>Gleophyllum trabeum</i>		<i>Poria placenta</i>		<i>Coriolus versicolor</i>	
	WL	MC	WL	MC	WL	MC	WL	MC
160°C, 6h, air	40.6	74.8	18.9	125.0	42.3	78.1	12.6	77.4
Control	35.3	76.5	15.3	122.2	42.9	74.7	12.8	90.9
160°C, 6h, water vapour	20.0	57.4	25.6	141.7	42.4	75.7	14.1	68.3
Control	32.3	65.2	21.9	106.9	40.5	68.4	14.1	84.9
160°C, 24h, air	0.8	65.0	2.5	74.8	4.8	33.8	3.4	68.5
Control	38.6	66.8	16.3	133.7	45.4	73.7	14.2	76.0
160°C, 24h, water vapour	26.4	57.9	23.6	104.1	46.5	63.1	12.2	68.4
Control	31.2	67.4	14.6	136.1	48.3	65.0	12.6	69.0

### **Biological resistance of wood modified at the temperature of 190°C for the period of 6 hours**

The above parameters of wood thermal treatment, both in the atmosphere of air and water vapour, increased wood resistance against the *C. puteana* fungus. Differences in weight losses between the examined experimental and control samples averaged 38% (Table 3). In the case of activities of the remaining test fungal species, no improvement in biological resistance was

observed. Differences in weight losses ranged from 1.1 to 8.2%. Moisture contents of modified samples after the mycological examination ranged from 48 to 105%.

### **Biological resistance of wood modified at the temperature of 190°C for the period of 24 hours**

Thermal treatment of wood, both in air and water vapour conditions, increased wood resistance against all species of tested fungi (Table 3). The greatest differences in weight losses of control and experimental samples were recorded in the case of activities of *C. puteana*, *G. trabeum* and *P. placenta* fungi. Differences in weight losses amounted to, respectively: 43, 15 and 19%, for samples modified in the atmosphere of air and to 37, 12 and 23%, for samples modified in the atmosphere of water vapour. The resistance of experimental samples against the *C. puteana* fungus was characterised by wood weight losses at the level of 2.7% (modification in air atmosphere) and 1.9% (modification in water vapour atmosphere). In the case of the remaining fungal species and both types of treatments, the respective values were: 3.3 and 3.6%; 27.9 and 23.8% and 10.7 and 5.9%. Wood moisture content after investigations ranged from 39 to 86%.

*Table 3: List of wood weight losses in the result of action of test fungi (WL, %) and wood moisture content (MC, %) in an agar-block test*

Process parameters	<i>Coniophora puteana</i>		<i>Gleophyllum trabeum</i>		<i>Poria placenta</i>		<i>Coriolus versicolor</i>	
	WL	MC	WL	MC	WL	MC	WL	MC
190°C, 6h, air	5.9	48.1	11.3	94.2	42.7	63.8	8.5	80.1
Control	44.5	84.2	18.8	123.4	45.7	69.4	12.7	77.0
190°C, 6h, water vapour	7.0	49.0	18.0	104.8	42.1	67.4	7.7	72.0
Control	44.2	74.7	19.1	111.9	43.3	74.7	15.9	90.1
190°C, 24h, air	2.7	59.6	3.3	66.0	27.9	49.0	10.7	43.1
Control	45.4	74.1	18.5	135.1	46.9	67.0	11.5	80.6
190°C, 24h, water vapour	1.9	38.7	3.6	85.7	23.8	43.2	5.9	77.2
Control	38.8	72.4	15.6	134.0	46.8	75.6	10.9	81.1

### **Biological resistance of wood modified at the temperature of 220°C for the period of 6 hours**

After thermal treatment in the above-mentioned conditions, wood showed high resistance against the action of test fungi. Weight losses of samples modified in air and water vapour atmospheres subjected to the action of *C. puteana*, *G. trabeum*, *P. placenta* and *C. versicolor* fungi amounted to, respectively: 0.8 and 1.1; 2.5 and 1.8; 4.8 and 8.9 and 3.4 and 3.2%. Wood moisture content after experiments ranged from 34 to 81% (Table 4).

### **Biological resistance of wood modified at the temperature of 220°C for the period of 24 hours**

The most extreme process conditions of wood thermal treatment led to the highest losses of weight. Similarly to the previous technological variant, the applied thermal treatment parameters turned out to be equally effective from the point of view of increasing wood resistance against the action of test fungi. The smallest sample weight losses due to decay were found in the case of wood modified in water vapour (Table 4). The recorded weight losses were either smaller than or did not exceed 3%, which, in the case of testing the effectiveness of wood preservatives, is close to their limiting fungicidal value. Weight losses of samples subjected to the action of *C. puteana*, *G. trabeum*, *P. placenta* and *C. versicolor* fungi amounted to, respectively: 1.3; 1.6; 2.2 and 3.0%. Weight losses of samples modified in air and subjected to the action of fungi were slightly

higher and amounted to: 1.6; 4.0; 2.2 and 4.7%. Wood moisture content after experiments ranged from 38 to 57%.

**Table 4: List of wood weight losses in the result of action of test fungi (WL, %) and wood moisture content (MC, %) in an agar-block test**

Process parameters	<i>Coniophora puteana</i>		<i>Gleophyllum trabeum</i>		<i>Poria placenta</i>		<i>Coriolus versicolor</i>	
	WL	MC	WL	MC	WL	MC	WL	MC
220°C, 6h, air	9.3	54.1	26.1	94.4	44.7	66.8	14.0	78.7
Control	37.4	72.5	17.5	116.8	43.8	68.3	15.7	69.8
220°C, 6h, water vapour	1.1	43.8	1.8	81.2	8.9	39.1	3.2	57.7
Control	40.0	66.7	23.7	130.0	54.2	78.9	9.9	54.0
220°C, 24h, air	1.6	38.6	4.0	53.4	2.2	46.0	4.7	40.0
Control	41.2	80.3	13.7	140.5	50.9	72.7	10.9	78.5
220°C, 24h, water vapour	1.3	47.4	1.6	70.8	2.2	37.7	3.0	56.7
Control	39.8	70.6	22.0	148.0	48.5	72.3	11.6	99.2

### Analysis of results

Biological resistance of thermally modified wood turned out to vary considerably. The extent of resistance to the action of test fungi, as expressed by the loss of wood weight caused by the action of a given test fungi, depended on the process conditions of the thermal treatment. Wood modified in relatively mild thermal air conditions ( $T = 160^{\circ}\text{C}$ ,  $t = 6\text{h}$ ) resulted in a 5% lower weight loss, in relation to non-modified wood for resistance against the action of *C. puteana* and *G. trabeum* fungi. The occurrence of this phenomenon can be attributed to a reduced extent of polymerisation of cellulose material during the process of thermal treatment. This was accompanied by a small wood weight loss which did not exceed 2%. This can further be explained by polymerisation reactions, which accompany the break down on non-cellulosic carbohydrates in temperatures below  $200^{\circ}\text{C}$ . Sugar anhydrides, mono- and oligo- as well as polysaccharides polymerise at temperatures above  $200^{\circ}\text{C}$  forming dextrans as well as other branched carbohydrates. This kind of carbohydrate material can be more easily available for fungi (Highley 1987). Above the temperature of  $200^{\circ}\text{C}$ , hemicelluloses undergo rapid break down which is accompanied by the formation of a wide range of various dehydration products, volatile organic compounds,  $\text{H}_2\text{O}$ ,  $\text{CO}$  and  $\text{CO}_2$  and carbon substance. The main constituent of hemicelluloses is xylan or its glycuronic derivatives. Products of the decomposition of these compounds, e.g. furfural, can form toxic compounds affecting the resistance of wood to biodegradation caused by fungi. Kamdem *et al.* (1999) maintain that increased resistance of wood modified at higher temperatures ( $T = 220^{\circ}\text{C}$ ) is also affected by trace quantities of lignin phenol derivatives. This was confirmed by the high resistance of wood modified at the most extreme experimental temperatures ( $T = 220^{\circ}\text{C}$ ,  $t = 24\text{h}$ ) against the activity of the *C. puteana* fungus, which was characterised by the highest cellulolytic activity. The second most aggressive fungus with respect to its corrosive properties causing smaller weight losses of modified wood was the *C. versicolor* fungus. This organism is capable of breaking down, apart from carbohydrates, the lignin complex contained in the wood cell wall (Erikson *et al.* 1990).

From the point of view of improving wood biological resistance, the parameter of thermal treatment duration as well as conditions in which the process took place (air / water vapour) played a secondary role in comparison with the temperature parameter. Nevertheless, the application of water vapour allowed removing from wood products of hemicellulose hydrolysis as indicated by the smell of the steamed wood as well as the colour of condensates after wood

hydrothermal treatment. In addition, this also confirmed the smallest weight loss in the result of the action of test fungi.

## CONCLUSIONS

1. Wood modified in the environment of water vapour at the temperature of 220°C and for 24 hours achieved resistance against test fungi. The obtained resistance complied with the requirements specified in EN 113 standard for wood protection agents.
2. Mild conditions of thermal treatment increased the sensitivity of modified wood to decomposition caused by fungi used in the mycological test.
3. *C. puteana* and *C. versicolor* fungi, of all the applied test fungi, were found to be the most aggressive towards modified wood.

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## Comparison of Properties of Wood Modified by 8 Different Methods – Durability, Mechanical and Physical Properties

H. Epmeier<sup>1</sup>, M. Westin<sup>2</sup>, A.O. Rapp<sup>3</sup> and T. Nilsson<sup>4</sup>

<sup>1</sup> Chalmers University of Technology, Steel and Timber Engineering, SE-412 96 Göteborg, Sweden.

E-mail address: hannah.epmeier@ste.chalmers.se

<sup>2</sup> Swedish Institute for Wood Technology Research (Träteknik), Box 5609, SE-114 86 Stockholm, Sweden.

E-mail address: mats.westin@tratek.se

<sup>3</sup> Bundesforschungsanstalt für Holzwirtschaft (BFH), Wood Biology and Wood Protection,

D-210 31 Hamburg, Germany. E-mail address: arapp@holz.uni-hamburg.de

<sup>4</sup> Swedish Univ. of Agricultural Sciences, Dept of Wood Science, SE-75007 Uppsala,

Sweden. E-mail address: thomas.nilsson@trv.slu.se

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### ABSTRACT

The durability, mechanical and physical properties of wood modified by eight methods were studied. The methods were: 1) Acetylation, 2) Maleoylation (using water solution of MG or ethanol solution of maleic anhydride), 3) Succinylation, 4) Furfurylation, 5) NMA-modification, 6) Modification with reactive linseed oil derivative (UZA), 7) Treatment with methylated melamine resin (MMF) and 8) Thermal modification.

Wood species used were Scots pine (*Pinus sylvestris*), Beech (*Fagus sylvatica*) and Birch (*Betula pubescens*). Both pure sapwood and heartwood specimens of pine were used. Methods 2-6 were part of the *Chemowood* project (FAIR-CT97-3187) and therefore each modification was performed by the project participant responsible for the method. Acetylation, furfurylation, MMF-treatment and heat treatment were performed by the authors at Chalmers University of Technology or at BFH in Hamburg. For laboratory decay testing in TMCs (soilboxes) and pure basidiomycete culture bioassays, the test specimens were cut from larger modified wood blocks. Some of the modification methods were also used to produce mini-stakes for field tests in three Swedish fields.

The following properties were studied: durability, dimensional stability, modulus of elasticity (MOE),  $\Delta$ MOE and stiffness stabilisation efficiency (SSE) when subjected to different climates, modulus of rupture (MOR), hardness and impact strength.

Some modification methods result in modified wood with poor durability, whereas other methods (acetylation, maleoylation, furfurylation and MMF-treatment) seem to provide excellent resistance to microbial decay. Generally, all modification methods result in reduced equilibrium moisture content and slightly increased dimensional stability. However, some modification methods such as acetylation and furfurylation lead to more pronounced improvements of these properties.

## INTRODUCTION

Many authors have reported on durability, mechanical and physical properties of thermally or chemically modified wood (Stamm 1964, Rowell 1984, Kumar 1994, Larsson 1998, Rapp 1999, Sailer *et al.* 2000). However, it is difficult to compare data when the wood material and testing methods are different. Therefore, an effort was made in this study to, as far as possible, compare a great number of modification methods applied to similar wood material (in most cases replicates) in the same test series and with respect to several important properties. Furthermore, in no study reported in literature, have so many methods been compared in so many property aspects as in this study.

## EXPERIMENTAL METHODS

### **Wood materials**

The main wood material used in the field tests was Scots pine (*Pinus sylvestris L.*). All modification methods were applied on pine sapwood. Most of the methods were also applied on beech (*Fagus sylvatica*) and birch (*Betula pubescens*), and a few on Norway spruce (*Picea abies*).

Concerning the pine, a distinction was made between pure sapwood and pure heartwood samples. The birch and the beech material as well as most of the Scots pine material were of unknown origin. The Scots pine came from the wood work shop at Chalmers. The birch and the beech came directly from the sawmill of AB Gustav Kähr, a parquet flooring manufacturer, Sweden.

Before modification, most of the material for physical and mechanical testing was cut to small specimens of the dimension 10x10x250mm with one exception: birch and beech were furfurylated as blocks of the dimension 70x40x450mm and then cut to test sample size. The test specimens of the Scots pine material were split into three groups with different year ring width. For the basidiomycete and TMC tests, wood specimens of the dimensions 150x50x60mm and 150x50x120mm, respectively, were sawn from one single beam of Scots pine, for most of the modification treatments. However, concerning the durability test, the acetylated wood came from the material of the detailed study described below and for melamine treatment and thermal treatment the wood material is described in IRG papers (Westin *et al.* 1997, Bengtsson *et al.* 2002).

In a more detailed study with pine and a few of the modification methods (acetylation, modification with methylated melamine formaldehyde resin, and heat treatment in oil), the Scots pine material came from a slow grown stand on the west coast of Sweden near Gothenburg. Each tree was cut into three logs (root, intermediate and top) then each log was cut into two parts. As much sapwood as possible was taken when sawing beams from the logs, one from each side. Each beam was then cut into studs with a cross section of 45 x 70 mm and a length of approximately 1500mm. The studs were marked by origin and position in the tree in order to facilitate the matching of treated specimens and controls.

### **Modification of wood**

Acetylation and furfurylation were performed in pilot plants at Chalmers University of Technology, whereas modification with MMF resin and oil heat treatment in pilot plants at BFH or Menz Holz. The remaining chemical modifications (maleoylation, succinylation, NMA-

modification and modification with reactive linseed oil derivative) were performed by the different partners of the *Chemowood* project (FAIR-CT97-3187). For the field and laboratory decay tests, pine and spruce from a Swedish sawmill were heat treated in a *Thermowood*<sup>®</sup> production plant by Stora-Enso in Finland. Pine that had been heat treated by the *NOW*<sup>®</sup> process in France, was also included in the field test.

### **Acetylation**

The acetylation was carried out at Chalmers according to Rowell *et al.* (1985), either in a 30 litre stainless steel reactor (small samples) by Hannah Epmeier or in a pilot plant with a microwave-heated 800 litre reactor (larger samples) by Dr Larsson-Brelid. Before being treated, the wood specimens were dried to a moisture content of about 5%. The time for heating-up in the pilot plant was 30 min, the reaction time was approximately 1h and the time for removal of residual chemicals was approximately 2h. The acetylation procedure is further described in Larsson (1998).

### **Maleoylation**

The maleoylation was carried out at VTT in Finland, either with water solution of MG (maleic anhydride esterified glycerol) or with maleic anhydride (MA) in ethanol solution. The MG was prepared by refluxing maleic anhydride and glycerol in 3:1 molar ratio for an hour. Two concentrations of aqueous MG-solution were used (20 and 15% MG), and one concentration of maleic anhydride in ethanol solution (15% MA). The samples were vacuum/pressure-impregnated with MG- or MA-solutions by full cell process. After the impregnation, all samples were subjected to: a pre-drying phase at 40°C (over night), a first reaction phase at 90°C (4h) and finally a second reaction phase at 170°C (4h).

### **Succinylation**

The succinylation was carried out at the BioComposites Centre in Wales with succinic anhydride (SA) in acetone solution, 7.5% or 15% SA. The wood samples were pre-dried over night in an oven at 105°C, transferred to a stainless steel pressure vessel, vacuum-impregnated with the acetone solution of succinic anhydride for 5 min, a 6 bar pressure was applied for 2h and pressure was released. The vessel was sealed and placed in an oven at 120°C for 2 hours. The reactor was then cooled down to room temperature in 30min and the wood blocks removed. The blocks were put in a drying cabinet at room temperature for an hour and then post-reacted/dried in an oven at 105°C over night.

### **Furfurylation**

The furfurylation was carried out at Chalmers. Modified specimens with different levels of PFA-loading (poly-furfuryl alcohol loading) were prepared. The PFA-loading was calculated as weight percent gain (WPG) due to modification. The four target levels for pine sapwood were: PFA<sub>A</sub>) 120% WPG (high level), PFA<sub>B</sub>) 60% WPG (medium-high level), PFA<sub>C</sub>) 30% WPG (medium-low level), and PFA<sub>D</sub>) 15% WPG (low level). The co-solvents used for all levels except the highest were either methanol (MeOH) or a mixture of methanol and fine spirit (95% ethanol in water) and the FA-concentrations in the four solutions were 92%, 48%, 30% and 15%. The catalysts used in low concentrations were citric acid, maleic anhydride, phthalic anhydride and triethanolamine.

Impregnation was performed according to the full cell process in a small stainless steel reactor (30-litre capacity). The vacuum step was applied for 45 min using a membrane pump, the treating solution was introduced and a pressure of 12 bar was applied for 2h by nitrogen gas. The

samples were wiped clean and weighed. In the case when co-solvent was used, the co-solvent was removed after impregnation (but prior to curing) in a vacuum drying oven using a temperature ramp starting at 20°C and ending at 40°C four hours later. The stakes were wrapped in aluminum foil and cured/reacted overnight in an oven at 103°C. In the morning the aluminum foil was removed and the stakes were post-cured/dried for another eight hours at 103°C in the oven. All surfaces of the stakes were sanded down slightly, in order to avoid the effect of PFA-coating.

#### **Modification with NMA**

The modification was carried out at Ghent University in Belgium with water solutions of n-methylol acrylamide (NMA) in three concentrations (6%, 12% and 24% NMA). The catalysts used were citric acid and aluminium nitrate. The wood samples were impregnated by full cell process, pre-dried at 40°C in a ventilated oven for 16h. The samples were then transferred to a reactor and reacted by raising the temperature gradually from 40°C to 110°C during 4h, with steaming periods (3 x 10 min) during the last hour, followed by drying in the ventilated oven over night.

#### **Modification with reactive linseed oil derivative (UZA)**

The modification was carried out at Stichting Hout Research (SHR) in the Netherlands. The treatment cycle for all specimens was 1) Wood specimens placed in a 30-litre capacity stainless steel reactor, 2) 30min vacuum step, 3) Introduction of treating liquid, 4) 45min pressure step, 5) 60min post-vacuum with three periods of 2min steaming. One set of wood specimens were treated with UZA with a standard addition (for linseed oils) of conventional Co/Zr-drier. The remaining specimens were treated with a UZA with 1% peroxide added.

#### **Treatment with methylated melamine formaldehyde resin (MMF resin)**

The modification was performed at BFH in Hamburg, Germany. The original water solution had a concentration of MMF-resin of 75%. To obtain the desired concentrations of 7.5% and 15% it was further diluted with water. The specimens were impregnated with the MMF-resin solution by full cell process with a vacuum step of 30 minutes and a 4-hour pressure step at 8 bar. After impregnation the small wood samples were allowed to dry for 48 hours at room climate and then placed in a drying cabinet at 30°C in which the temperature was raised by 20°C every 24 hours until a temperature of 140°C was reached. This temperature was kept for 4 hours to secure a sufficient curing of the resin. The large wood samples were stored for about four months, after MMF-impregnation, in a storage room with outdoor climate conditions. Then they were kiln dried and cured in the same way as the pilot study material but only for 2 hours at 120°C.

#### **Thermal modification**

All wood samples for mechanical and physical testing and part of the samples for durability testing were oil heat treated (OHT) in rape seed oil in a small pilot plant at BFH (small specimens) or in the production plant at Menz Holz (large specimens) in Germany. The samples were treated at 160°C and 190°C. At BFH a bath of rapeseed oil was heated overnight at atmospheric pressure until the desired temperature was reached and the specimens were submerged in the hot oil. The treatment time was 8 hours at 160°C and 4 hours at 190°C, respectively. The specimens were taken out of the oil bath and allowed to cool down at room temperature. In the large plant the wood specimens were treated according to two production treatment programmes with peak temperatures of 160°C and 190°C, respectively, during 4h. A general description of this process is given in Sailer et al. (2000). As the hydrophobic effect of oil in the wood surface was not part of the experiment, the exposed surfaces were cut away 1mm

in depth before testing. This was done in order to reduce the influence of hydrophobation. For durability tests, wood specimens were also taken from 4m beams heat treated by the *Thermowood*-process in the production plant of Stora-Enso in Honkalahti, Finland. In this plant, the wood was heat treated in saturated steam with a process peak temperature of 220°C. In field tests, pine heat treated by the *NOW*-process in a pilot plant in St. Etienne, France, was also included.

### ***Preparation of test specimens***

#### **Preparation of test specimens for durability testing**

At least 5 mm of surface material was removed on all sides on all modified wood blocks, in order to avoid edge effects in the following testing. For basidiomycetes tests, each of the slightly smaller blocks was cut into 32 test-specimen (5x15x30mm), of which eight were saved for repeating trials in case one of the pure cultures would not provide high enough weight loss of untreated controls. Each of the slightly larger blocks was cut into 30 test specimen (5x10x100mm) for TMC tests. Except for acetylated and thermally modified wood samples, all the TMC-sticks and half the number of blocks for pure culture bioassay testing were leached by an altered version of EN84. The alteration meant leaching for one week with methanol, which was exchanged with fresh methanol five times, they were then leached in de-ionised water for one week with change of water five times. The remaining half of pure culture test samples were leached according to ordinary EN84, *i.e.* two weeks in water which was exchanged to fresh de-ionised water 10 times. The reason for using an altered leaching procedure for most of the blocks was an attempt to remove possible low-molecular fungicidal hydrophobic compounds, which may remain in the wood after water leaching. Examples of such compounds could possibly be monoesters and di-esters formed between maleic anhydride and ethanol which were expected to be found in maleoylated and furfurylated wood. By comparing the results from bioassay tests of blocks leached in different manners, these effects could be studied. The TMC test of acetylated, thermally modified and CCA-treated samples was started one year after the main test and these samples were not leached since earlier trials had revealed that there were no statistical difference in performance of such modified specimens, leached or non-leached. For field tests the mini-stakes, 8x20x200mm, were prepared from larger modified wood blocks in the case they had not been prepared before modification.

#### **Preparation of test specimens for mechanical and physical testing**

After the treatment, each of the 250mm long specimens for the screening study were sawn into specimens with the dimension of 10x10x200mm and two specimens for impact bending test, 4x8x45mm. To simplify the measurements on the small sticks in the longitudinal direction, a hole was drilled in the middle of the cross section at both ends and a small rivet was inserted (these rivets had to be taken into account when measuring length and weight). All specimens were subjected to conditioning at a temperature of 23°C and a relative humidity of 65% for four weeks. A total amount of 491 specimens were included in the screening study. At the average a set of 10 small sticks was prepared for each modification and level (cf. table 1).

#### **1500mm studs:**

After a treatment, in most cases the studs had to be planed again to the original size of the cross section (45x70mm). From the studs bending creep specimens were cut to a length of 1100 mm. From the remaining part of each stud a 200mm long piece was taken for sawing small specimens (10x10x200mm) from the whole cross section. At the average 18 small specimens per cross section were obtained. Some samples had to be sorted out because of knots or vane. The bending

creep specimens and the corresponding smaller specimens were subjected to conditioning at a temperature of 23°C and a relative humidity of 65% for four weeks. At the end of the conditioning period all specimens were weighted and the MOE was measured by eigenfrequency.

**Table 1: Screening study – Number of small specimens per modification and level**

<b>Modification method/modification chemical</b>	<b>pine sap</b>	<b>pine heart</b>	<b>spruce</b>	<b>birch</b>	<b>beech</b>
controls	20	12	36	4	6
Acetylation with acetic anhydride (Ac)	10	10	18	10	10
Treatment with MMF-resin (MMF)	10	10	-	10	10
Ac+MMF	10	10	-	10	10
Oil heat treatment at 160°C (OHT 160)	5	6	9	6	8
Oil heat treatment at 190°C (OHT 190)	5	6	9	6	8
High level of furfurylation (Falc A)	10	-	-	-	-
Medium-high level of furfurylation (Falc B)	10	10	-	12	-
Medium-low level of furfurylation (Falc C)	10	10	-	-	11
Lowest level of furfurylation (Falc D)	10	-	-	-	-
Modification with MG in low conc (MG low)	10	-	-	2	8
Modification with MG in higher conc (MG high)	10	-	-	-	-
Mod. with succinic anhydride in low conc (SA low)	10	10	-	1	9
Mod. with SA in higher conc (SA high)	10	-	-	-	-
High level of modification with UZA (UZA high)	10	10	-	3	7
High level of modification with UZA (UZA high)	10	-	-	-	-
High level of modification with NMA (NMA high)	10	10	-	5	5
Low level of modification with NMA (NMA low)	10	-	-	-	-
<b>Σ</b>	<b>180</b>	<b>104</b>	<b>36*</b>	<b>79</b>	<b>92</b>

*\* identical material for controls and treated specimens*

Before loading, the bending creep specimens were end-sealed to simulate long spans in view of moisture diffusion and steel plates were attached to hold the suspension devices in place.

For each bending creep test sequence, a total of 36 bending creep specimens was prepared with six specimens connected in series to a set. For each specimen the side nearest to the pith was always positioned in the tension zone.

**Table 2: Detailed study – Number of bending creep specimens and number of corresponding smaller specimens per modification and level**

	<i>bending creep specimens (studs)</i>	<i>10x10x200mm specimens</i>
<i>Acetylated (Ac)</i>	<b>12</b>	<b>216</b>
<i>Controls to Ac</i>	<b>12</b>	<b>216</b>
<i>MMF 15%</i>	<b>15</b>	<b>270</b>
<i>MMF 7.5%</i>	<b>12</b>	<b>216</b>
<i>Controls to MMF</i>	<b>12</b>	<b>216</b>
<i>OHT 160</i>	<b>12</b>	<b>216</b>
<i>OHT 190</i>	<b>12</b>	<b>216</b>
<i>Controls to OHT</i>	<b>12</b>	<b>216</b>
<i>untreated</i>	<b>9</b>	<b>162</b>
<b>Σ</b>	<b>108</b>	<b>1944</b>

A bending creep test included 12 controls and 12 modified specimens per modification level. When only one modification level was prepared (as was the case with acetylated wood) the remaining test places were filled up with more controls or untreated specimens.

The difference between untreated specimens and controls lies in the drying procedure. The controls for respective modification were dried and conditioned in exactly the same way and at the same time as the treated specimens. The untreated specimens underwent no special drying. After being sawn they were stored at room climate and then joined in for the conditioning procedure.

A total amount of 108 bending creep specimens and 1944 corresponding smaller specimens were included in the second part of the study (*cf.* table 2).

### ***Durability testing***

#### **Laboratory testing in pure basidiomycete cultures and terrestrial microcosms (TMC)**

Modified wood specimens (5x15x30mm) were exposed to monocultures of basidiomycetes for 16 weeks after which the percentage weight loss was calculated. The basidiomycetes were *Postia placenta* (brown rot fungus) and *Coriolus versicolor* (white rot fungus). The 5x10x100mm-specimens were buried to  $\frac{3}{4}$  of their length in the soil in three types of terrestrial microcosms, TMCs. These were: a compost soil (TMC 1), soil from the Simlångsdalen test field (TMC 2) and soil from a conifer forest (TMC 3). The characteristics conifer forest soil resembled the characteristics of the soil in the Ingvallsbenning test field. Specimens were removed after 6 and 12 months after which the weight loss was calculated.

#### **In-ground field tests (“graveyard tests”) with mini-stakes**

Mini-stakes (8x20x200mm) were put out in ground contact in three test fields, buried to  $\frac{3}{4}$  of their length. The fields were located in: Simlångsdalen in the south of Sweden, Ultuna, 500 km northeast of Simlångsdalen and Ingvallsbenning, another 100 km northwest of Ultuna. Simlångsdalen is a field with dominating brown rot decay. Ultuna is a fertile field with dominating soft rot and bacterial decay and Ingvallsbenning is an acidic conifer forest field with a dominant white rot decay. Mini-stakes were also put out in ground contact in a subterranean termite field in Bogor, Indonesia. These stakes were also buried to  $\frac{3}{4}$  of their length.

For the Swedish fields the rating was done in accordance with the European standard EN 252, in which no decay (sound) is rated 0, slight decay 1, moderate decay 2, severe decay 3 and failure is rated 4. An Index of Decay was calculated from the average rating figures of each group of stakes, when rated according to the standard. In this system an index of 0 means that all stakes are sound and 100 means that all stakes have failed.

For each stake in the Indonesian field the weight loss due to termite attack was calculated and expressed as percentage of the original weight.

#### **Field test in sea water with marine borer activity (according to EN 275)**

A full-scale marine test according to EN 275 was started with furfuryl alcohol modified wood at four modification levels, acetylated wood, MMF-resin treated wood at two modification levels and wood heat treated by different processes. Five or six specimens each of succinylated (with or without post-impregnation with copper sulphate), UZA modified and maleoylated wood were included in the trial as screening test of some different processes. Reference treated wood was two levels of NWPC Standard No.1 (2.6% and 0.6% water-free CCA salt in water solution) and durable tropical wood (*Minquartia guyanensis*). In January 1999, all specimens were put out on rigs close to the sea bottom near Kristineberg Marine station, Northwest of Gothenburg.



**Testing of dimensional stability**

Anti-swelling efficiency (ASE) has been calculated in the fifth cycle when cycling between dry climate (RH30%, 20°C) and humid “outdoor” climate (RH90%, 20°C). The duration time for each cycle was four weeks, so the total time for the test was 24 weeks, including a four-week post-conditioning step at RH65%. The weight, length and thickness, in both radial and tangential direction, was measured before each climate-change and from these values the swelling constants and ASE-values could be calculated. The size for the test specimen was 10x10x200 mm (rad x tan x long) and the reason for this was to also enable the measurement of the vibrational modulus of elasticity and to perform static bending test at the end of the test. The wood material of the test stakes was pine sapwood and heartwood, and to minor extent beech and birch. Although this resulted in less statistic basis for the calculated ASEs for beech and especially birch, it made it possible to indicate the properties of modified birch for comparison with the other more thoroughly investigated species. However, for modification with furfuryl alcohol the number of beech and birch test specimen within each group was higher (11 and 12, respectively) than for the other modification methods.

**Mechanical testing****Vibrational modulus of elasticity (MOE) and Stiffness Stabilisation efficiency (SSE)**

The modulus of elasticity was measured in two ways: non-destructively at 30% and at 90% RH and finally destructively at 65% RH. For the non-destructive method, the eigenfrequency in the longitudinal direction was used. At each climate, the weight and dimensions of each stake were measured and density calculated, after which the eigenfrequency was measured by hitting the stake with a small hammer and analysing the response via a microphone. Based on eigenfrequency ( $f$ ), length ( $l$ ) and density ( $\rho$ ), the MOE was calculated according to Eq. 1 (Bengtsson 1999).

$$\text{MOE} = 4 \cdot \rho \cdot f^2 \cdot l^2 \quad [\text{N/mm}^2] \quad (1)$$

This was performed in both climates in the fifth cycle, as discussed in the part with dimensional stability. Modification changes not only the MOE in absolute figures from untreated to treated condition but it also has an influence on the changes in MOE when the same (treated) material is subjected to different humidities. The MOE for each sample was measured in both climates and the difference, the  $\Delta\text{MOE}$  was calculated according to Eq. 2. Usually the MOE is higher at 30% RH, if it is the other way round, the  $\Delta\text{MOE}$  becomes negative.

$$\Delta\text{MOE} = \text{MOE}_{30} - \text{MOE}_{90} \quad (2)$$

In order to quantify the stiffness stabilisation efficiency of a modification, a ratio, the SSE expressed as percentage [%], was calculated according to Eq. 3.

$$\text{SSE} = \frac{\Delta\text{MOE}_{\text{untreated}} - \Delta\text{MOE}_{\text{treated}}}{\Delta\text{MOE}_{\text{untreated}}} * 100 \quad [\%] \quad (3)$$

where the  $\Delta\text{MOE}_{\text{treated}}$  is the average  $\Delta\text{MOE}$ -value for each group of modified stakes and the  $\Delta\text{MOE}_{\text{untreated}}$  is the average  $\Delta\text{MOE}$ -value of the unmodified stakes. The higher the SSE value the higher the stabilisation effect of the modification. An SSE value of, for example, 26% means that the MOE of the modified material differs 26% less between the two climates than the MOE of the unmodified material does. A negative SSE value indicates that the treatment made the material more sensitive to moisture changes ( $\Delta\text{MOE}$  in the treated conditions was higher than in the untreated).

**Static bending test**

According to the EN standard for testing of mechanical properties for timber structures (EN 408:1995) the stakes were tested to failure in 4-point bending after which the MOE and modulus of rupture (MOR) could be calculated.

**Impact bending strength (by Charpy pendulum method)**

The testing of impact bending strength,  $A_w$  [kJ/m<sup>2</sup>], was performed according to standard ISO 3348 except that the required dimensions of 20 x 20 x 300 mm for the test specimens could not be met due to the size of the small specimens. The actual size came closer to the size specified in the ASTM standard D4508 (Chip impact strength of plastics). Each 4x8x50mm specimens was conditioned and tested at 65% RH. Two different annual ring orientations were tested to estimate the influence of the annual ring orientation. Due to the smaller sample size the values obtained were much lower than  $A_w$  values reported in literature (approximately 25% of the reported values from testing fully according to ISO 3348). However, the relative decrease in impact strength due to modification was believed to be relevant.

$$A_w = \frac{1000 * Q}{b * h} \quad [\text{kJ/m}^2] \quad (4)$$

The impact bending strength was calculated according to Eq. 4 where  $Q$  is the energy required for fracture of the test piece, in joules, and  $b$  and  $h$  are the dimensions of the test piece in the radial and tangential directions, in millimetres.

**Brinell hardness**

After being conditioned at 65% RH the specimens were subjected to the testing procedure according to standard EN 1534 except that the sample size of approximately 50 mm side length recommended by the standard could not be met due to the dimensions of the sticks (10 x 10 x 200 mm).

$$HB = \frac{2 * F}{\pi * D * (D - (D^2 - d^2)^{0.5})} \quad [\text{N/mm}^2] \quad (5)$$

The applied load  $F$  was 1000 N for all wood species. On each specimen four measurements were made, two on the radial surface and two on the tangential surface. The hardness,  $HB$  [N/mm<sup>2</sup>], was calculated according to Eq. 5 where  $D$  the diameter of the indenter, and  $d$  the diameter of the lasting indentation.

**Bending creep in cyclic climate variation**

For the bending tests, in principle the same equipment was used as described by Bengtsson (1999). The studs were loaded flat wise by suspending a load of ca 180 kg which generated a bending stress of 10 N/mm<sup>2</sup> in each stud. The deflection was measured by LVDT-gauges in the middle of the constant moment area. The relative creep was calculated based on deflection after 60 seconds. The deflection values were recorded each hour with a PC-based data logging. The relative creep was defined as deflection at a given time divided by the deflection after 60 seconds.

**RESULTS AND DISCUSSION*****Durability*****Laboratory tests with pure basidiomycete cultures**

The results from testing in bioassays with pure brown rot and white rot fungi can be seen in the right-hand columns (weight loss caused by *Postia* and *Coriolus*, respectively) of tables 3 and 4.

Prior to the test the samples were leached and the resulting weight losses can be seen in the middle column. For all modification methods, except modification with UZA, there were only minor differences found between the decay weight losses of the samples leached in water and those leached in methanol half of the leaching period. Therefore average decay weight loss figures are given although the specimen had been leached in two ways.

**Table 3: Results in laboratory bioassays for wood modified by all chemicals except UZA.**

Modification type (/chemical)	Modification level	Weight loss during leaching	Weight loss after 16 weeks in Bioassay 1 (brown rot) <i>Postia placenta</i>		Weight loss after 16 weeks in Bioassay 2 (white rot) <i>Coriolus versicolor</i>	
		(%)	Weight loss (%)	std.	Weight loss (%)	std.
<b>Leached 2 weeks in water (aq) or 1 week MeOH + 1 week in water</b>						
aq / MeOH+aq						
<b>None (Control)</b>	untreated	<b>1.5 / 2.4</b>	<b>69.10</b>	± 0.85	<b>31.85</b>	± 2.75
	Acetone-extracted	<b>1.7 / 1.9</b>	<b>68.52</b>	± 1.46	<b>33.46</b>	± 1.62
<b>NMA</b> (n-metyhylo- acrylamide)	WPG = 6.5	<b>3.9 / 5.0</b>	<b>42.25</b>	± 5.97	<b>8.72</b>	± 2.48
	WPG = 13.7	<b>4.8 / 5.5</b>	<b>34.26</b>	± 6.27	<b>4.78</b>	± 1.07
	WPG = 27.6	<b>4.9 / 6.1</b>	<b>13.46</b>	± 2.25	<b>4.34</b>	± 0.20
<b>Succinylation</b> (succinic anhydride)	WPG = 13.6	<b>1.9 / 2.2</b>	<b>27.92</b>	± 3.37	<b>4.11</b>	± 0.69
	WPG = 23.9	<b>1.9 / 2.1</b>	<b>14.01</b>	± 1.61	<b>2.91</b>	± 0.37
<b>MG (aq)</b> (maleic anhydride esterified glycerol)	WPG = 9.6	<b>1.5 / 1.8</b>	<b>30.48</b>	± 4.10	<b>4.43</b>	± 0.53
	WPG = 16.4	<b>1.0 / 1.2</b>	<b>17.68</b>	± 1.71	<b>3.74</b>	± 0.19
<b>MA (EtOH)</b> (maleic anhydride)	WPG = 8.8	<b>1.1 / 1.2</b>	<b>3.52</b>	± 3.66	<b>0.15</b>	± 0.16
-----						
<b>Control to Falc, MMF and CCA</b>		not measured	<b>52.5</b>		<i>Phanerochaete chrysosporium</i> <b>20.0</b>	
<b>FAlc</b> (furfuryl alcohol)	WPG < 25	not measured	<b>7.4</b> (3.1 - 10.7)		<b>4.7</b> (2.6 - 6.0)	
	WPG > 100	not measured	<b>1.9</b> (1.0 - 3.8)		<b>2.8</b> (2.2 - 4.0)	
<b>MMF-resin treatm</b>	WPG = 52	not measured	<b>1.6</b>		<b>4.2</b>	
<b>CCA</b>	9 kg/m <sup>3</sup>	not measured	<b>4.0</b>		<b>1.1</b>	

**Table 4: Results in laboratory bioassays for wood modified by UZA.**

Modification type (/chemical)	Modification level	Weight loss during leaching	Weight loss after 16 weeks in Bioassay 1 (brown rot) <i>Postia placenta</i>		Weight loss after 16 weeks in Bioassay 2 (white rot) <i>Coriolus versicolor</i>	
		(%)	Weight loss (%)	std.	Weight loss (%)	std.
<b>Leached 2 weeks in water</b>						
<b>UZA</b> (reactive linseed oil derivative)	WPG = 18.2	<b>3.57</b>	<b>32.75</b>	± 5.29	<b>3.73</b>	± 0.63
	WPG = 23.4	<b>3.21</b>	<b>23.64</b>	± 2.51	<b>3.58</b>	± 0.06
	WPG = 30.0	<b>3.82</b>	<b>21.73</b>	± 3.11	<b>4.54</b>	± 0.84
<b>Leached 1 week in methanol followed by 1 week in water</b>						
<b>UZA</b> (reactive linseed oil derivative)	WPG = 18.2	<b>11.60</b>	<b>40.99</b>	± 1.65	<b>15.94</b>	± 1.39
	WPG = 23.4	<b>15.74</b>	<b>37.93</b>	± 1.80	<b>16.48</b>	± 1.78
	WPG = 30.0	<b>17.65</b>	<b>52.65</b>	± 2.30	<b>11.49</b>	± 0.99

In the bottom of table 3 (below the marking line) results from earlier studies have been included for comparison. All the modification methods seem to have an inhibiting effect on white rot fungus, as can be seen in the column to the right in table 3. However, only maleic anhydride modified wood (0.15% weight loss) and succinylated wood (2.91%) seemed perfectly sound in the same way as wood modified with furfuryl alcohol at high level of modification had performed in the earlier trials (2.8% weight loss). In the brown rot bioassay, only three of these were effective: maleic anhydride (3.52% weight loss), MMF-resin (1.6% WL) and furfuryl alcohol (1.9% for high levels of modification and 7.4% for low levels in the earlier trials). MG in water solution was not as effective although some inhibiting effect could be noted at the higher WPG and the same was valid for NMA and succinylation. Concerning UZA (table 4), there were large differences between the samples leached in water only and the ones also leached in methanol – it seems that almost all the weight that had been gained due to the modification was lost in the leaching step (compare the upper group in middle column in table 3 with the lower). However, none of the UZA-groups performed well in brown rot bioassay tests.

### Laboratory tests with terrestrial microcoms (TMC)

*Table 5: Results for modified pine sapwood after 12 months in 3 different TMCs.*

Modification type (/chemical)	Modification level	Weight loss during leaching %	Weight loss in TMC 1 (Compost soil) 12 months expo		Weight loss in TMC 2 (Simlångsdalen soil) 12 months exposure		Weight loss in TMC 3 (Conifer forest soil) 12 months exposure	
			Weight loss (%)	St.Dev. (%)	Weight loss (%)	St.Dev. (%)	Weight loss (%)	St.Dev. (%)
<b>Control I &amp; II</b>	untreated	<b>2.35</b>	<b>77.97</b> ± 3.64		<b>62.86</b> ± 3.40		<b>20.12</b> ± 1.96	
	Acetone-extracted	<b>2.14</b>	<b>76.68</b> ± 9.46		<b>58.49</b> ± 3.53		<b>14.77</b> ± 2.63	
<b>NMA</b> (n-metyhylol-acrylamide)	WPG = 7.9	<b>2.89</b>	<b>5.40</b> ± 1.04		<b>5.19</b> ± 2.00		<b>4.29</b> ± 0.73	
	WPG = 14.8	<b>2.43</b>	<b>1.90</b> ± 0.67		<b>3.05</b> ± 0.53		<b>3.96</b> ± 0.25	
	WPG = 26.4	<b>2.06</b>	<b>0.45</b> ± 0.22		<b>2.76</b> ± 0.18		<b>3.12</b> ± 0.20	
<b>UZA</b> (reactive linseed oil)	WPG = 1.5	<b>3.75</b>	<b>78.83</b> ± 5.23		<b>62.62</b> ± 2.34		<b>15.65</b> ± 0.58	
	WPG = 23.3	<b>11.45</b>	<b>46.60</b> ± 2.46		<b>49.43</b> ± 7.11		<b>12.06</b> ± 0.51	
	WPG = 26.8	<b>15.53</b>	<b>40.16</b> ± 3.45		<b>43.47</b> ± 7.63		<b>9.87</b> ± 1.26	
<b>Succinylation</b> (succinic anh.)	WPG = 8.8	<b>1.27</b>	<b>2.09</b> ± 2.43		<b>2.01</b> ± 0.16		<b>2.82</b> ± 0.34	
	WPG = 20.2	<b>1.12</b>	<b>1.66</b> ± 0.28		<b>2.87</b> ± 0.11		<b>2.68</b> ± 0.36	
<b>MG (aq)</b> (maleic anhydr. esterified glvc.)	WPG = 9.1	<b>1.69</b>	<b>2.61</b> ± 1.03		<b>3.30</b> ± 0.28		<b>5.54</b> ± 1.08	
	WPG = 16.2	<b>0.76</b>	<b>1.91</b> ± 0.53		<b>3.14</b> ± 0.33		<b>3.01</b> ± 0.51	
<b>MA (EtOH)</b> (maleic anhydr)	WPG = 7.2	<b>1.41</b>	<b>0.62</b> ± 0.18		<b>1.60</b> ± 0.15		<b>1.40</b> ± 0.43	
<b>Falc</b> (furfuryl alc.)	WPG = 22	<b>2.41</b>	<b>5.69</b> ± 1.60		<b>5.19</b> ± 1.63		<b>8.54</b> ± 0.53	
	WPG = 41	<b>1.69</b>	<b>2.12</b> ± 0.71		<b>2.78</b> ± 0.34		<b>4.99</b> ± 0.74	
	WPG = 60	<b>0.57</b>	<b>1.05</b> ± 0.84		<b>1.76</b> ± 0.09		<b>1.89</b> ± 0.38	
<b>Control III</b>	untreated	not leached	<b>94.50</b> ± 11.61		<b>41.87</b> ± 17.68		<b>17.08</b> ± 7.82	
<b>Acetylated</b>	21% acetyl	not leached	<b>0.40</b> ± 0.27		<b>0.65</b> ± 0.33		<b>0.44</b> ± 0.25	
<b>Heat treated</b>		not leached	<b>5.42</b> ± 1.44		<b>1.91</b> ± 0.19		<b>2.67</b> ± 0.48	
<b>CCA (NWPC-Standard no.1)</b>	4 kg/m <sup>3</sup> (class AB)	not leached	<b>42.76</b> ± 11.94		<b>5.40</b> ± 4.33		<b>2.89</b> ± 0.60	
	9 kg/m <sup>3</sup> (class A)	not leached	<b>25.21</b> ± 5.15		<b>2.14</b> ± 1.57		<b>1.28</b> ± 0.38	
<b>Control IV</b>		not measured	<b>49.7</b>		<b>60.5</b>		<b>57.6</b>	
<b>MMF-resin</b>	WPG = 52	not measured	<b>3.1</b>		<b>3.1</b>		<b>4.1</b>	

The results from TMC testing in three types of soils can be seen in the right-hand columns (weight loss caused by decay) of table 5. Prior to the test the samples were leached and the resulting weight losses can be seen in the third column. There was no significant difference between the untreated and the acetone extracted pine sapwood. For all modification methods, except modification with UZA, there were only minor differences found between the weight losses from leaching of the control samples and leaching of the modified samples (see 3<sup>rd</sup> column of table 5).

Already after 6 months test, the pine controls were severely decayed in the compost soil ( $\approx 60\%$  WL) and the Simlångsdalen soil (61% WL) but only slightly decayed in the conifer forest soil (7.4% WL). However, all modified wood samples (except UZA-treated) were quite sound with weight losses below 3%. In table 5 the results after 12 months are shown. The weight loss for the controls are about the same in TMC 2 (62.86%), but higher in TMC1 (almost 80% WL) and TMC3 (20.12% WL) when compared with the results after 6 months exposure.

Again, no significant efficacy by UZA-modification can be seen. For the lowest levels of modification with NMA, and Falc weight losses of 4-6% (and in the case of Falc in TMC3 even 8.54%) indicates poorer performance than the 6-month data could reveal. For all succinylated, MG-modified, NMA-modified samples at medium and high level and Falc-modified at medium level, better decay resistance can be noted with weight loss values between 1.0 and 2.9%. The best performance could be seen for samples modified by MA (maleic anhydride) and Falc at high modification level (WPG=60) with weight loss values between 0.6 and 1.9%. In the supplementary test with acetylated, thermally treated (Thermowood) and CCA-treated wood, the weight loss of the controls was slightly lower in TMC2 (41.87% WL) and TMC3 (17.08% WL) compared to the first study but the WL in TMC1 was very high (94.50%). The performance of CCA treated wood was very poor at low CCA retention level (42.76% WL) in the compost soil (TMC1) and rather poor even at high retention level (25.22% WL). The performance of thermally treated wood in TMC1 (5.42% WL) and TMC2 (1.91% WL) was better than CCA, whereas the WL was slightly higher (2.67%) in TMC3. However, the performance of acetylated wood was excellent in all TMCs with eight losses below 1%. The MMF-resin modified wood was tested in a separate study where TMC3 soil came from the Ingvallsbenning field. The WL of the controls were much higher in this type of soil (57.6% WL) than the controls in the TMC3 soils in the other studies. The WL in TMC2 was about the same (60.0) as in the first study, whereas the WL in the compost soil (TMC1) was lower (49.7%). The performance of the MMF-resin modified wood was rather good in all TMCs.

### **In-ground field tests with mini-stakes in Sweden**

As an example of the field performance of modified wood mini-stakes (8x20x200mm) the data for 5 years in the Simlångsdalen field is given in table 7. In this field all controls have failed, with an average service life of 2.0 years. All of the CCA-treated stakes at the low retention level except one had failed and the remaining stake was severely decayed. Succinylated stakes are performing very poorly, and heat treated, MMF-treated at low retention level and furfurylated stakes at low modification levels are performing rather poorly. However, acetylated, MMF-treated at high retention level and furfurylated stakes at medium and high retention levels, were still sound.

A comparison of the performance of modified wood mini-stakes in Simlångsdalen with the performance in Ultuna and Ingvallsbenning is shown in table 8. Although the decay type is very different in these three fields, the performance of acetylated, furfurylated and MMF-treated wood is quite similar in all three fields. At the higher modification levels these modification methods seem to provide a performance equal to or better than CCA in the retention level approved for use in HC4, 9 kg/m<sup>3</sup> (based on crystal water free salt, which corresponds to 12 kg/m<sup>3</sup> based on preservative product). However, the thermally modified wood does not perform

similarly in the different fields – in Ultuna all heat treated stakes were sound whereas in Simlångsdalen some stakes had failed and others were severely decayed.

**Table 7: Condition of pine sapwood mini-stakes (8x20x200mm) after 5 years in the old Simlångsdalen test field.**

Wood treatment	Chemical Retention		Number of stakes	No. of stakes classified as			Index of Decay (0-100)	Average Service life (years)
	WPG	(kg/m <sup>3</sup> )		sound	decaying	rejected		
Acetylation	25		7	7	-	-	0	-
Acetylation + MMF-treatment	25+4		6	6	-	-	0	-
Succinylation	11		9	1 <sup>c</sup>	-	8	89 <sup>c</sup>	-
Succinylation+CuSO <sub>4</sub> -low	11+	0.2kg Cu	4	-	-	4	100 <sup>c</sup>	1.0 <sup>c</sup>
Succinylation+CuSO <sub>4</sub> -high	11+	0.6kg Cu	6	-	3 <sup>c</sup>	3 <sup>c</sup>	88 <sup>c</sup>	-
Furfurylation	15		6	1	3	2	54	-
	33		4	2	2	-	31	-
	50		6	6	-	-	0	-
	>100		6	6	-	-	0	-
MMF-resin treatment	8		9	-	9	-	42	-
	15		9	5	4	-	14	-
	30		9	7	2	-	6	-
Heat treatment <sup>d</sup>	-	-	10	4	2	4	55	-
NWPC <sup>a</sup> Standard No.1 (CCA)		2.1 <sup>b</sup>	16	-	3	13	91	-
		9.0 <sup>b</sup>	16	14	2	-	6	-
Untreated controls	-	-	35	-	-	35	100	2.0

<sup>a</sup> Nordic Wood Preservation Council <sup>b</sup> CuO (19 wt-%); CrO<sub>3</sub> (36 wt-%); As<sub>2</sub>O<sub>5</sub> (45 wt-%) <sup>c</sup> One year exposure <sup>d</sup> in the new field

**Table 8: Condition of pine sapwood mini-stakes (8x20x200mm) after 5 years in three Swedish fields.**

Chemical treatment	Chemical retention		Index of Decay (0-100% decay)		
	WPG	(kg/m <sup>3</sup> )	Simlångsdalen	Ultuna	Ingvallsbenning
Acetylation	17-18% acetyl		48	38	38
	19-21% acetyl		12	22	5
	23% acetyl		0	12 <sup>d</sup>	
Succinylation	11		89 <sup>c</sup>	0 <sup>c</sup>	33 <sup>c</sup>
Succinylation + CuSO <sub>4</sub> -low	11	+0.2kg Cu	100 <sup>c</sup>	0 <sup>c</sup>	40 <sup>c</sup>
Succinylation + CuSO <sub>4</sub> -low	11	+0.6kg Cu	88 <sup>c</sup>	0 <sup>c</sup>	4 <sup>c</sup>
Furfurylation	15		54	38	67
	50		0	12	12
	>100		0	0	0
MMF-resin treatment	8		42	33	40 <sup>d</sup>
	15		14	25	
	30		6	0	
Thermal modification	-		55	0	35
NWPC <sup>a</sup> Standard No.1 (CCA)		2.1 <sup>b</sup>	91	80	84
		9.0 <sup>b</sup>	6	33	3
Untreated controls	-	-	100	100	100

<sup>a</sup> Nordic Wood Preservation Council <sup>b</sup> CuO (19 wt-%); CrO<sub>3</sub> (36 wt-%); As<sub>2</sub>O<sub>5</sub> (45 wt-%) <sup>c</sup> One year exposure

<sup>d</sup> 25x50x500mm-stakes with 20.6% acetyl content

The succinylated stakes have only been in test for one year, but since the performance is so poor in two of the fields (Simlångsdalen and Ultuna), it is probably only a matter of time until decay starts also in the remaining field (Ingvallsbenning).

### **In-ground mini-stake tests in fields with high subterranean termite activity**

The performance of acetylated and high-furfurylated wood was very good – all these stakes were sound after one year in the Bogor field whereas very little of the control stakes remained (93% weight loss). In a supplementary test of furfurylated stakes in the Bandung field, medium-furfurylated wood (WPG=43) also seemed to be resistant to termite attack.

**Table 9: Performance of pine sapwood mini-stakes (8 x 20 x 200 mm) in Indonesian termite fields**

Modification method	Bogor field, Weight loss (%)			Bandung field, Weight loss (%)		
	3 months	6 months	1 year	3 months	6 months	1 year
Control (untreated Pine sap)	33	47	93	10	66	85
MMF-resin treatm - WPG = 6	4	25	89	-	-	-
- WPG = 10	0	3	63	-	-	-
Furfurylation - WPG = 15	3	16	62	4	62	65
- WPG = 43	-	-	-	0	0	0
- WPG =115	1	1	2	0	0	0
Acetylation - 22% acetyl	1	1	2	-	-	-
Acetylation+MMF - WPG=24+4	0	1	1	-	-	-

### **Marine field tests (EN 275)**

All untreated pine sapwood samples in the first set of controls were rejected at the assessment after one year (see table 10, column to the right). They were so heavily attacked by *Teredo navalis* (shipworms) that the *teredo* tunnels covered more than 90% of the X-ray pictures. They were replaced with new controls and at each assessment during the forthcoming years all controls had failed due to *teredo* attack and were replaced. The UZA modified samples and one set of heat treated samples were also rejected after only one year due to heavy teredo attack. However, the acetylated samples, the acetylated samples post-treated with furfuryl alcohol or MMF-resin, one set of oil heat treated samples, the MMF-resin treated samples at medium and high modification level and the furfurylated samples at medium to high modification level were all rated sound after 3 years of test.

### ***Mechanical and physical testing***

#### **Equilibrium moisture content (EMC)**

The equilibrium moisture content is reduced by all methods studied (cf. figure 1), however to different extent. The reduction due to modification with reactive linseed oil derivative (UZA) and treatment with methylated melamine resin (MMF) only leads minor reduction in EMC. However, furfurylation at medium modification level (Falc B) leads to a reduction in EMC by 2/3 and acetylation leads to an even stronger reduction. Furthermore, the levels of EMC were approximately the same for modified birch and beech.

**Table 10: Condition of pine sapwood samples (25 x 75 x 200 mm) after 3 years of exposure on test rigs in the bay outside Kristineberg Marine Research Station.**

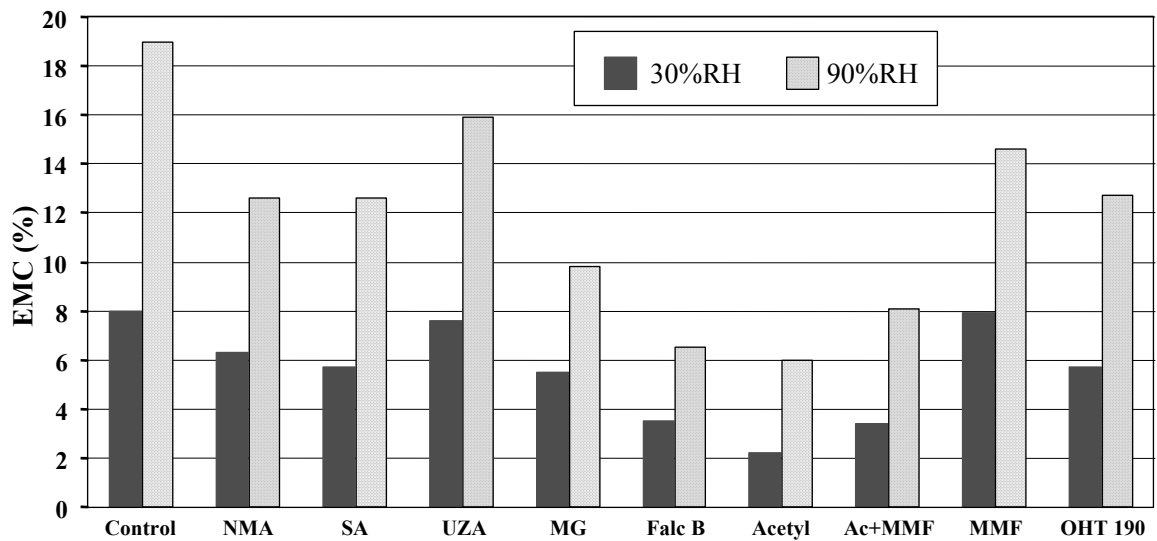
Wood treatment chemical	Chemical retention		No. of stakes	No. of samples classified as			Rating, Terenid attack (0-4)	Overall rating	Aver. Service life (years)
	WPG	(kg/m <sup>3</sup> )		sound	attacked	rejected			
Furfuryl alcohol (Falc)	11		5	-	5	1	3.0	Severe	-
	29		5	5	-	-	0.0	Sound	-
	50		5	5	-	-	0.0	Sound	-
	120		5	5	-	-	0.0	Sound	-
Succinic anhydr. (SA)	13		1	-	-	1	4	Failed	2
	24		1	-	1	-	2	Moderate	-
SA + Cu	17-32	5 (Cu)	3	1	2	-	0.7	Slight	-
Maleic anhydride or MG	17-44		4	1	3	-	1.0	Slight	-
Acetic anhydride (Ac)	21% AC		5	4	1	-	0.2	Sound	-
Ac + MMF	21+ 8		5	5	-	-	0.0	Sound	-
	21+19		5	5	-	-	0.0	Sound	-
Ac + Falc	19+ 7		3	3	-	-	0.0	Sound	-
	19+18		3	3	-	-	0.0	Sound	-
MMF resin	11		4	-	4	-	2.0	Moderate	-
	23		4	4	-	-	0.0	Sound	-
	47		4	4	-	-	0.0	Sound	-
UZA	?		2	-	-	2	4.0	Failed	1.0
None (Thermal modification A)	-		6	-	-	6	4.0	Failed	1.0
None (Thermal modification B)	-		5	-	-	5	4.0	Failed	1.4
None (Thermal modification C)	-		5	5	-	-	0.0	Sound	-
CCA (NWPC <sup>a</sup> Standard No.1)		4 <sup>b</sup>	6	-	1	5	3.8	Failed	-
		18 <sup>b</sup>	6	6	-	-	0.0	Sound	-
Untreated pine sap controls	-	-	8+5+5	-	-	8+5+5	4.0 <sup>c</sup>	Failed <sup>c</sup>	1.0 <sup>c</sup>
Untreated <i>Minquartia g.</i>	-	-	5	5	-	-	0.0	Sound	-

<sup>a</sup> Nordic Wood Preservation Council

<sup>b</sup> CuO (19 wt-%); CrO<sub>3</sub> (36 wt-%); As<sub>2</sub>O<sub>5</sub> (45 wt-%)

<sup>c</sup> Three sets, each lasted

1 year



**Figure 1: Equilibrium moisture content (EMC) for pine sapwood modified by 9 different methods.**



**Anti-swelling efficiency (ASE)**

The volumetric ASE is high for acetylation, furfurylation and maleoylation (MG) represented by high bars in figure 2. For the other methods the ASE is more moderate.

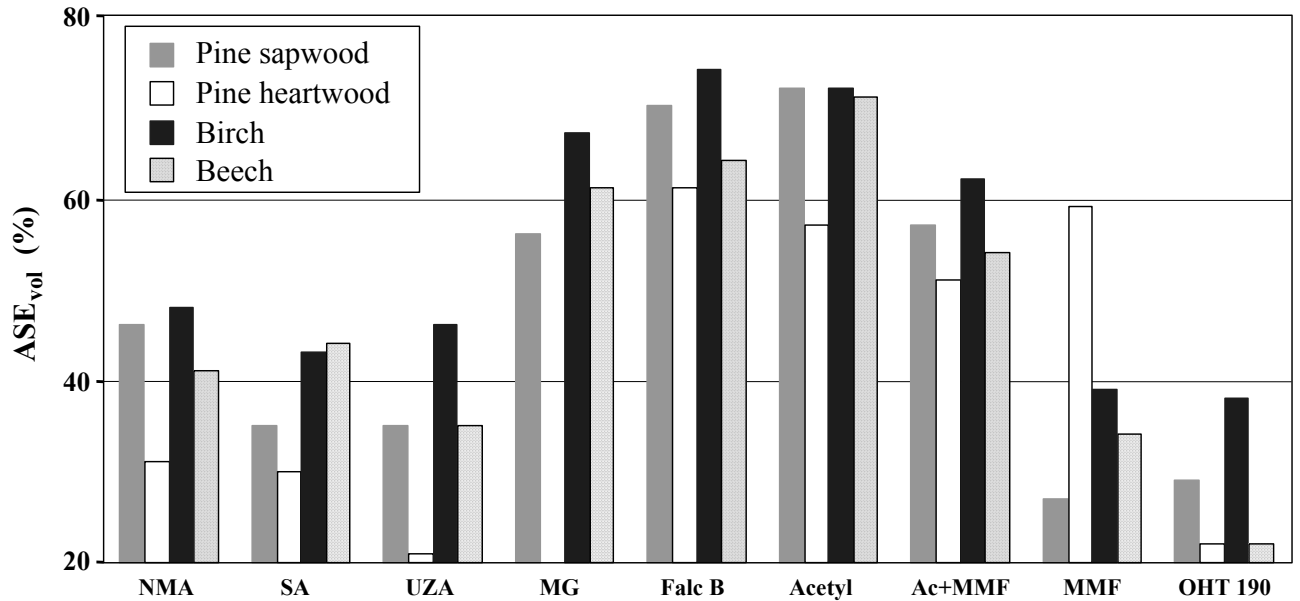


Figure 2: Volumetric anti-swelling efficiency (ASE<sub>vol</sub>) of 9 modification methods on 4 types of wood material.

In the longitudinal direction the ASE is more modest, and actually quite similar for the different modification methods as can be seen in figure 3. Modification with NMA, SA (succinylation), MMF and OHT (oil heat treatment) results in longitudinal ASEs which comes close to the volumetric ASEs. However, MG-modification, furfurylation and acetylation seem to have lower stabilising effect on the longitudinal swelling compared to the tangential and radial swelling, resulting in lower ASE<sub>long</sub> than ASE<sub>vol</sub>.

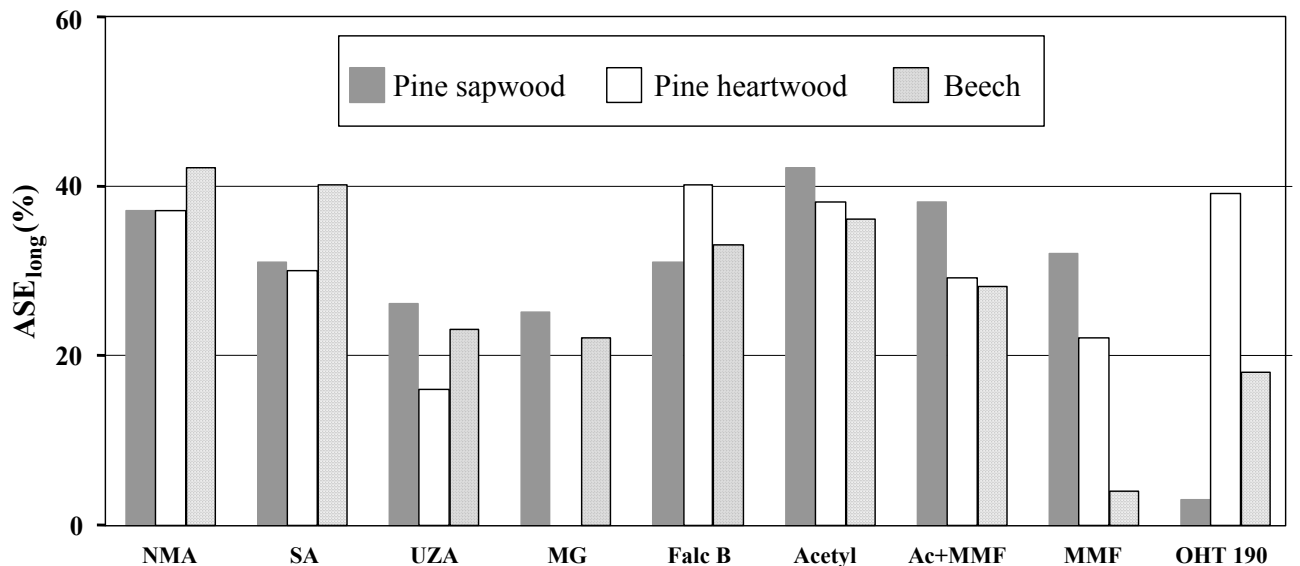


Figure 3: Longitudinal anti-swelling efficiency (ASE<sub>long</sub>) of 9 modification methods on 3 types of wood material.

**Stiffness stabilisation efficiency (SSE)**

As can be seen in table 11 and figure 4, the SSE of succinylation and modification with NMA is practically zero, which means that succinylated and NMA-modified wood softens as much as

untreated wood does when subjected to moist climate. Modification with UZA, MMF-treatment and oil heat treatment gives a low but slightly positive SSE (8-20%). Maleoylation and acetylation followed by MMF treatment gives a somewhat higher SSE (30-60%). The degree of furfurylation decides the SSE: at the lowest modification level the SSE is rather modest (28%), whereas at medium levels the SSE is between 50 and 65%. The SSE for high furfurylation level was not tested, but is believed to be higher than 65%. The SSE for acetylation was high (67-77%), meaning that the MOE changes very little when the climate changes – the stiffness is relatively independent of the relative humidity in the air.

*Table 11: Stiffness stabilisation efficiency, SSE, when cycling between dry climate (RH30%, 23°C) and “outdoor” humid climate (RH90%, 23°C) and impact strength at RH65%.*

Modification Type (chemical)	WPG	$\Delta$ MOE RH30 - RH90 (GPa)	SSE	Impact strength		Decrease in Impact Strength (%)
			(Stiffness Stabili- sation efficiency) (%)	RH65 (kJ/m <sup>2</sup> )	(std.)	
Untreated (control)	-	1.66	-	16.0	±2.8	-
NMA modification	8	1.63	+ 2	8.9	±2.4	45
	38	1.69	- 2	4.1	±1.0	75
Succinylation	6	1.65	± 0	11.0	±2.9	31
	12	1.64	+ 1	8.9	±1.5	44
UZA-modification	20	1.52	+ 8	12.0	±3.4	25
	42	1.51	+ 9	10.4	±3.2	35
Maleoylation (with MG-solution)	12	1.01	+ 32	4.2	±0.8	74
	20	1.12	+ 39	2.8	±0.8	83
Furfurylation	15	1.19	+ 28	11.0	±1.6	31
	32	0.72	+ 57	6.9	±1.0	57
	47	0.60	+ 64	6.4	±1.1	60
	137			5.6	±1.2	65
Acetylation <i>Acetyl. + MMF</i>	20	0.51	+ 69	15.7	±2.8	1
	19+5	0.79	+ 53	10.2	±3.4	36
MMF-resin treatm.	15	1.36	+ 18	6.3	±1.0	61
Oil Heat treatm (160)	34	1.49	+ 10	12.3	±4.4	23
Oil Heat treatm (190)	18	1.46	+ 12	11.9	±2.8	26

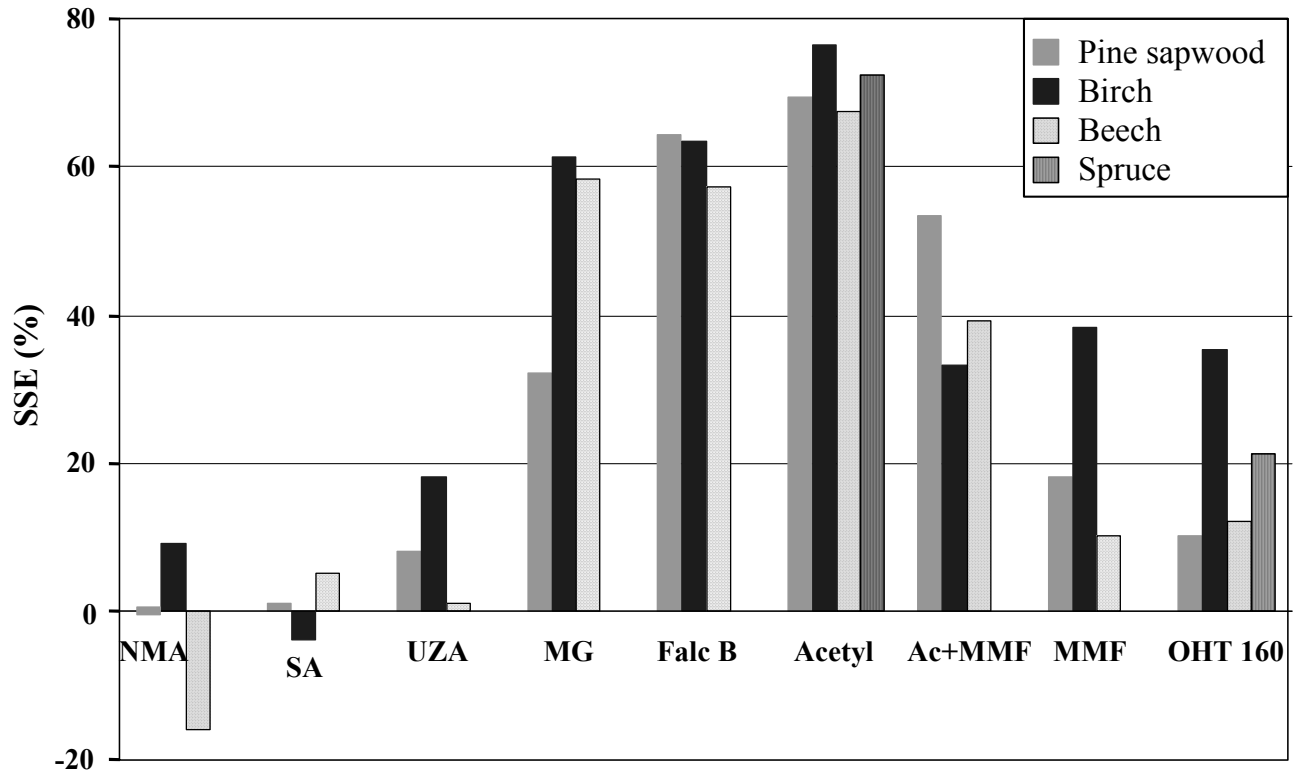


Figure 4: Stiffness stabilisation efficiency (SSE) of 9 modification methods on 4 types of wood material.

### Impact strength

When modifying Scots pine, all modification methods except acetylation leads to a reduction of the impact strength, *i.e.* an embrittlement, as can be seen when studying the grey and white bars in figure 5. However, the reduction in impact strength is minor for modification with UZA, whereas the reduction is quite severe due to modification with MG (>80% reduction). For the other methods the reduction is about the same (30-70%). For modified beech and birch specimens the values of impact strength reduction were similar to the values obtained for modified pine, except for acetylation and oil heat treatment which resulted in higher reduction (although selection of wood was not quite matched with the controls in those cases, which makes these values less certain). However, one should bear in mind that the test specimen size was very much smaller than specified in the EN standard and that this lead to impact strength values of control specimens which were only one quarter of the values achieved when testing specimens with the correct size. Furthermore, it is our belief that the small specimen size may have an even worse influence on specimen with lower impact strength, causing higher values of reduction than would have been the case if the proper test specimen size were used.

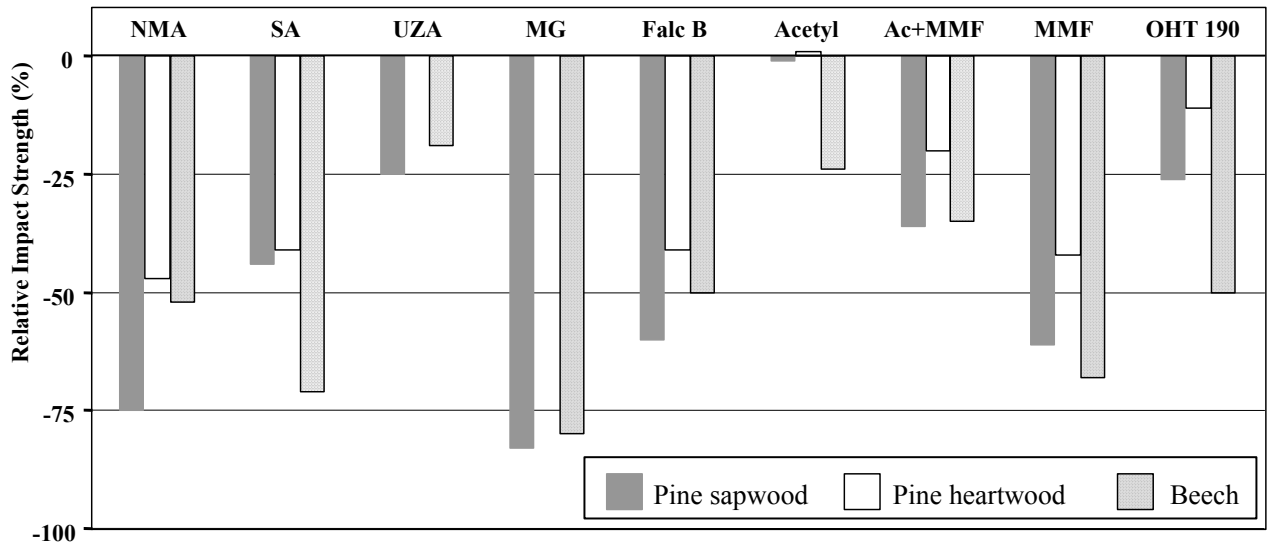


Figure 5: Relative decrease in impact strength due to modification of different wood materials.

### **Bending strength (MOR)**

The change in modulus of rupture (MOR) by the modification was in most cases not significant. In the case of acetylation, MMF-resin treatment, and furfurylation, the average MOR was slightly increased (approx. 10% increase). The MOR of UZA-treated and low-succinylated wood is approx the same as for controls. However, modification with NMA, MG<sub>low</sub> and oil heat treatment at 160C leads to a decrease in MOR by 10-20%, high-succinylated and oil heat treated at 190C to a decrease by 20-25% and finally MG<sub>high</sub> leads to a decrease in MOR by 1/3.

### **Brinell hardness (HB)**

All modification methods lead to increased hardness. However, the only modification method that leads to significant hardness increase was furfurylation – at high levels of furfurylation the increase was more than 100%. High levels of MMF-resin modification of wood is also believed to result in substantial hardness increase, but such specimens were not included in the test.

### **Bending creep**

Typical examples of relative creep curves are given in figures 6 and 7.

There are no significant differences in deflection between controls, acetylated and MMF-resin treated studs, although the deflection curves of the acetylated studs are more flat and with slightly lower values than the controls and MMF-resin treated. However, in relative creep, the differences between the controls and the acetylated studs are significant (cf. Figure 6). The curves of the acetylated studs are very flat with hardly any amplitudes, whereas the controls follows typical mechano-sorptive curves with clear amplitudes in each climate cycle.

Similar to the acetylated studs, the relative creep of the MMF-resin treated studs is significantly lower than the controls (cf. figure 7). However, only at the slightly higher level of modification (15% MMF), the curves have similar flat appearance that those of the acetylated have.

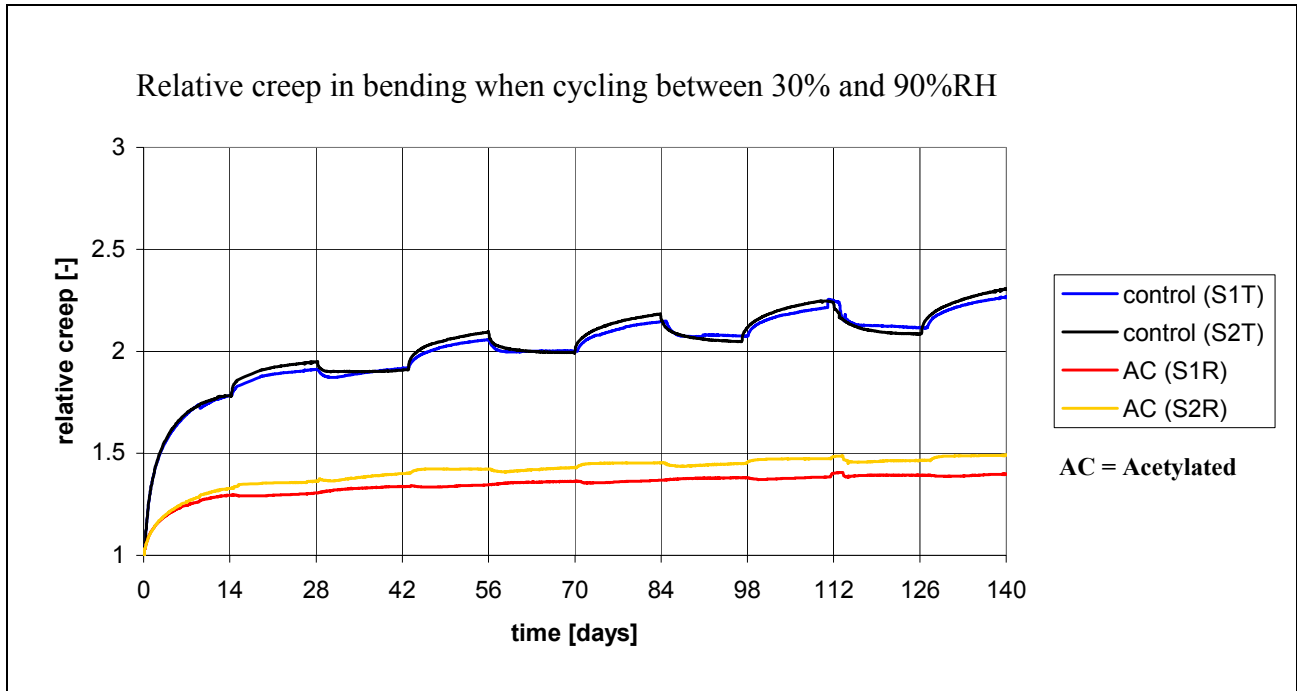


Figure 6: Relative creep in bending for acetylated studs compared to controls.

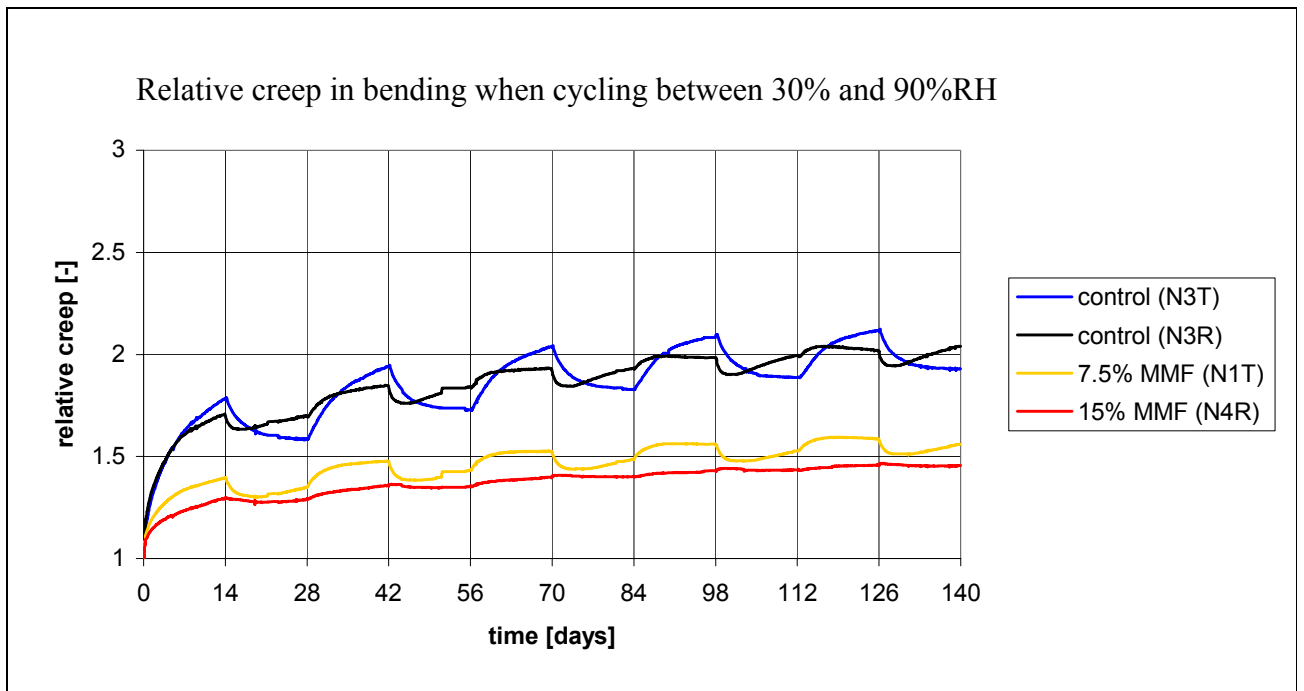


Figure 7: Relative creep in bending for MMF-resin treated studs compared to controls.

## CONCLUSIONS

There were only three modification methods that performed equal to or better than CCA-preserved wood (for HC4 use) in both laboratory decay tests and in all field tests – *Acetylation*, and at medium to high modification levels: *furfurylation* and *MMF-resin* treatment. Maleoylation (especially as modification with maleic anhydride in ethanol solution) was efficient in preventing decay in laboratory tests but not marine borer attack in marine field test. Acetylation and furfurylation were the most efficient modification methods for achieving high

dimensional stability, high SSE and low equilibrium moisture content. The relative creep in bending was substantially reduced by both acetylation and MMF-resin treatment. The impact strength of pine was decreased by all methods except acetylation, however to varying extent. Acetylation, furfurylation and MMF-resin treatment seems to lead to slightly increased bending strength, whereas most of the other methods seem to result in decreased bending strength. Finally, furfurylation at high degree of modification was the only method that resulted in substantially increased hardness.

### ACKNOWLEDGEMENTS

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## Decay of Anhydride Modified Wood

C.A.S. Hill<sup>1</sup>, M.D. Hale<sup>1</sup>, M.R. Farahani<sup>1</sup>, S. Forster<sup>2</sup>, E.D. Suttie<sup>3</sup>, D. Jones<sup>3</sup>, and A.N. Papadopoulos<sup>4</sup>

<sup>1</sup> School of Agricultural and Forest Sciences, University of Wales Bangor, Gwynedd, LL57 2UW, UK

<sup>2</sup> Arch Timber Protection, Technical Centre, Wheldon Road, Castleford, West Yorkshire, WF10 2JT, UK

<sup>3</sup> Centre for Timber Technology and Construction, BRE, Garston, Watford WD2 7JR

<sup>4</sup> Technical Educational Institute of Karditsa, Dept. of Wood and Furniture Technology Design, 43100, Karditsa, Greece.

**Keywords:** Acetylation, anhydride, fungal decay, brown rot, white rot, soft rot

### ABSTRACT

Protection against fungal attack is afforded by the chemical modification of wood. Many studies have been performed, particularly with acetylated wood, which have established decay protection thresholds. Despite these numerous studies, there is no real understanding of the mechanism by which decay protection occurs. This paper considers the various mechanisms proposed. Results are reported of recent studies of wood modified with anhydrides of different chain lengths tested against soft, brown and white rot fungi. With brown rot, the degree of OH substitution is not important in determining decay resistance. With soft rot, the level of substitution appears to be of importance at low weight percent gain levels, but not at higher levels of substitution. With white rot, lower levels of substitution are required to provide full decay protection. These results are discussed and possible decay protection mechanisms presented.

### INTRODUCTION

It is well established that the chemical modification of wood is able to provide protection against fungal attack (Rowell 1983, Hon 1996). A chemical modification reaction involves the formation of a chemical bond between a reagent and the cell wall polymers of wood. In almost all cases, this reaction occurs between some of the hydroxyl groups of these polymers and the reagent molecules. Such a reaction leads to a change in the chemical and physical properties of the substrate. For example, the acetylation of wood results in the substitution of hydrophilic hydroxyl groups with hydrophobic acetyl groups. In addition, the bonded adduct occupies additional space in the cell wall, over and above that which was occupied by the proton of the hydroxyl group. Thus, such a chemical reaction also results in an increase in dimensions of the reacted wood species, because of swelling of the cell wall. In most cases, chemically modified wood has a lower capacity for water absorption, with a lower equilibrium moisture content at a specified atmospheric relative humidity, when compared with unmodified wood.

In order that fungal attack can occur on wood, it is essential that the substrate can be metabolised by the fungi, and that the substrate has a moisture content above a certain threshold level (of the order of 20% moisture content) (Eaton and Hale, 1993). Several mechanisms can be postulated for the protection afforded by wood modification:

- The enzymes associated with metabolising the cell wall polymers are not able to recognise the substrate because the hydroxyl groups have been substituted.



- The moisture content of the cell wall is not sufficiently high for fungal attack to occur.
- Blocking of the cell wall micropores by bonded adduct prevents access to the cell wall interior.

#### ***Fungal enzymes and the cell wall of wood***

The decay of wood by micro-organisms requires the access of degradative agents to the interior of the cell wall. In brown-rot decay, the polysaccharide component of the cell wall polymers is extensively depolymerised before much weight loss has occurred (Kirk and Highley, 1973). With white rot, no extensive cellulose degradation occurs during the initial stages of decay, with the lignin being preferentially decomposed and removed. Various enzymes are held to be responsible for the decomposition of the cell wall polymers, but if they are to be involved in the decay processes they must gain access to the interior of the cell wall. Cellulases isolated from different decay fungi vary in molecular weight but typical dimensions, based on these molecular weights are *ca.* 5.0 nm if spherical and 3.3 x 20 nm if ellipsoidal (Cowling and Kirk, 1976). Xylanase has been shown to have an approximate diameter of 7 nm (Green *et al.*, 1989). Lignin peroxidases have dimensions of 4.7 nm (spherical) or 4.3 nm x 6.0 nm (ellipsoidal) (Flournoy *et al.*, 1993). However, it has been established in numerous studies that the cell wall micropores of undecayed wood have diameters no greater than 2 nm (Hill and Papadopoulos, 2001).

It is therefore apparent that during the initial stages of decay, these enzymes are not capable of penetrating the cell wall (Cowling and Brown, 1969). This has been verified by various studies of the distribution of enzymes using electron microscopy combined with labelling methods. By using immuno-gold labelling, it has been shown that lignin peroxidase does not penetrate the cell wall of undegraded wood (Daniel *et al.*, 1989; Srebotnik *et al.*, 1988).

#### ***The role of diffusible low molecular weight degradative agents***

Because of the lack of accessibility of enzymes to the cell wall interior, various low molecular weight degradative agents have been proposed as being the primary mechanism for initial decomposition of the cell wall polymers. During this process pore occluding substances, such as hemicelluloses and lignin, are progressively degraded, thereby allowing access of the enzymes into the cell wall interior. In brown rot decay, a Fenton's type system has been proposed as the method by which polysaccharide depolymerisation occurs (Murmamis *et al.*, 1987). More recently, this has been disputed and alternative mechanisms proposed (Green and Highley, 1997, Kerem *et al.*, 1999).

#### ***Decay and cell wall microporosity***

It is well known that the cell wall of wood contains an extensive network of microvoids, which exist because of the incomplete filling of space by the cell wall polymers. This network is often referred to as transient, since these microvoids collapse when wood is dried. Any process involving reaction with, or utilisation of the cell wall polymers, requires that the agent responsible gains access to the interior of the cell wall via the microvoid network. As noted above, these microvoids in sound wood have diameters no greater than 2 nm. Thus, in order that enzymes can penetrate the cell wall, it is necessary that the dimensions of the microvoids are increased by some process. Despite the obvious importance of this phenomenon, it has been little studied.

In a study of the brown rot decay of sweetgum using solute exclusion, it was shown that the micropore volume in the cell wall increased (from 0.35 cm<sup>3</sup>/gm to 0.7 cm<sup>3</sup>/gm) during decay, but there was no increase in micropore size (Flournoy *et al.*, 1991). The results suggested that the depolymerising agent must be smaller than 2.0 nm in diameter. In a parallel study of white rot decay of sweetgum, it was found that the cell wall pore volume increased from 0.35 cm<sup>3</sup>/gm to

0.6 cm<sup>3</sup>/gm, with an accompanying increase in maximum pore diameter from 2.0 nm to 5.0 nm (Flournoy *et al.*, 1993). Forster (1998), used solute exclusion to investigate the extent of cell wall micropore blocking due to acetylation. These results showed that there was lower accessibility into the cell wall due to acetylation, but even modification up to a weight percentage gain (WPG) of 20% did not prevent access by solute molecules smaller than 2.0 nm in diameter.

#### ***Chemical modification and decay resistance***

Many studies have been performed investigating the biological degradation resistance of acetylated wood to fungi, and other organisms. It is generally reported that a weight percentage gain of *ca.* 20% is required before full protection is achieved. Goldstein *et al.* (1961) acetylated Ponderosa pine using acetic anhydride in xylene. The modified wood was tested against six basidiomycete fungi, five brown rot and one white rot, with a weight percent gain (WPG) of 18% reported to be sufficient to provide decay resistance.

Peterson and Thomas (1978), acetylated loblolly pine, green ash and yellow poplar using acetic anhydride in xylene. The modified samples were tested against the brown rot fungus *Gloeophyllum trabeum* and the white rot fungus *Coriolus versicolor*. It was found that the white rot was generally easier to control than the brown rot, with levels of acetylation as low as 7% being able to provide protection. However, ash was still degraded by white rot, even at WPG levels of 20%. It was stated that 'blocking of action of fungal catalysts appears to be the primary protection mode of the acetylation technique'. Levels of acetylation of 17-20% (WPG) were generally found to provide full decay protection (with the exception of ash).

The effect of the level of acetylation on the decay resistance of Japanese red pine, red beech and albizzia was studied by Takahashi *et al.* (1989). Modified samples were exposed to the brown rot fungi *Tyromyces palustris*, *Serpula lacrymans*, the white rot fungus *C. versicolor* and to soft rot in unsterile soil. Protection against *T. palustris* was observed in all wood species at a WPG of 20%. With *C. versicolor*, a WPG of 6% was sufficient to protect softwood, but hardwoods required a WPG of 16%.

Beckers *et al.* (1994), determined the decay protection threshold levels for acetylated Scots pine to a variety of wood decay fungi. It was found that WPG levels of 18% were required against *Coniophora puteana* and *G. trabeum*, and 11% was required in an unsterile soft rot test. With the white rot fungus *C. versicolor* a zero weight loss was recorded at a WPG of 12%. However, even at a WPG level of 20%, full protection to *Postia placenta* was not achieved. A low moisture content of the wood due to modification was not thought to explain the protection against decay, since the modified wood has a moisture content of 60% after the fungal tests. It was stated that the water content of the cell wall might be low, but this was not thought to be a significant factor in inhibiting attack.

In ground contact stake tests of acetylated pine samples, it was found that an acetyl content of 20 % prevented attack by brown, white and soft rot fungi (Larsson Brelid *et al.*, 2000). Laboratory unsterile soil tests on acetylated mini-stakes showed that an acetyl content of 18.5 % was able to provide significant protection against fungal attack.

Vapour phase acetylated makamba (*Betula maximowiczii*) was exposed to a brown (*T. palustris*) and white rot (*C. versicolor*) fungus (Ohkoshi *et al.*, 1999). Mass loss due to decay with the brown rot fungus was zero at 20 % WPG, and with the white rot fungus at 12 % WPG.

Protection against soft rot attack (as measured by strength loss) has been reported for a WPG of 10.7 % for pine, 14.4 % for poplar and 12.8 % for beech (Beckers *et al.*, 1995).

In an extensive study of the decay of wood modified with a variety of reagents, Forster (1998) found that acetylation to a WPG of 17% provided full protection against the white rot fungi *C. versicolor* and *Pycnoporus sanguineus*, and a WPG of 24% with the brown rot fungi *C. puteana*, and *G. trabeum*. Tests were performed in low and high moisture content environments, with little difference in the thresholds.

Suttie *et al.* (1999), modified Scots pine with acetic, propionic, butyric, or hexanoic anhydrides and determined decay resistance against the brown rot fungi *C. puteana*, *G. trabeum*, *P. placenta* and a white rot fungus (*C. versicolor*) using European Standard method EN113 and a vermiculite overlay method. Resistance to soft rot attack was also determined using a modified ENV 807 stake test in unsterile soil. The effect of different levels of reaction upon decay resistance was only tested with the soft rot experiment. In this, it was found that a threshold of *ca.* 23% was required to ensure protection, regardless of the anhydride used.

#### **Wood swelling and wood decay**

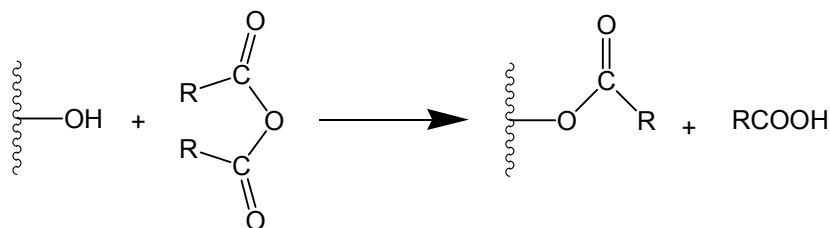
As noted above, the chemical modification of wood results in swelling of the material because the bonded adduct occupies space within the cell wall. This results in improved dimensional stabilization of the wood when it is exposed to moisture, because the wood is already pre-swollen to some extent. In addition, since the bonded adduct occupies space within the cell wall, there is as a consequence less space that can be occupied by the water molecules, resulting in reduced water uptake. Other treatments, such as resin-impregnation, thermal treatment, or formaldehyde cross-linking also result in improved dimensional stabilization. In the case of resin-impregnation, the resin molecules occupy space within the cell wall, although in this case no reaction occurs between the resin and the cell wall polymers. However, the mechanism for dimensional stabilization is similar to that for acetylation. With formaldehyde cross-linking, the reaction linking adjacent cell wall polymers prevents further expansion of the wood, when exposed to moisture. With thermal treatment, loss of hemicelluloses lowers the hydrophilicity of the material, and there is some evidence that greater cross-linking within the lignin framework also occurs.

Stamm and Baechler (1960) studied the decay resistance of wood treated by impregnation with phenol-formaldehyde resin, by formaldehyde cross-linking, acetylation, or thermal treatment. The relationship between weight loss due to fungal decay (*G. trabeum*) and reduction in swelling of the wood due to these treatments was investigated. A zero weight loss due to decay was recorded at swelling reductions of 60-70% with the resin treatment and acetylation, at around 40% with thermal treatment and 50 % with formaldehyde treatment. As a result of this study, the authors suggested that at these values of swelling reduction, the cell walls contained insufficient moisture to support decay.

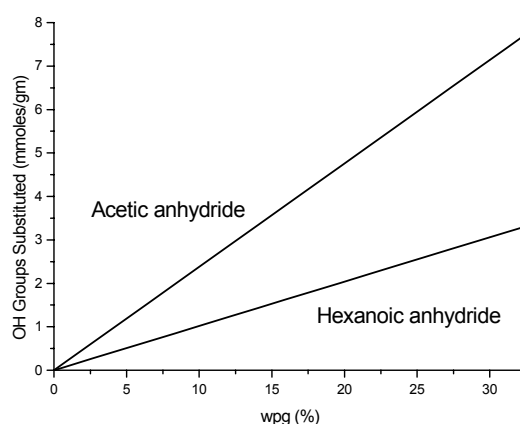
#### **Cell wall hydroxyl groups and wood decay**

According to Rowell (1982), at a WPG of 20% all of the lignin OH groups are substituted, whilst 48% of the accessible OH groups of the holocellulose are substituted. Investigations by Ohkoshi and co-workers using NMR methods, have shown that hemicellulose is preferentially substituted in acetylation reactions, with cellulose participating in reactions only above a WPG of 20%. Full substitution of the hemicellulose OH groups was found to occur only at a WPG of 35%, whereas free OH groups were detected on the lignin even at a WPG of 27% (Ohkoshi and Kato, 1993, 1997; Ohkoshi *et al.* 1997). Determination of the distribution of acetyl groups in the cell wall of wood or plant fibres has shown that the S2 layer shows the highest levels of substitution at

moderate WPG's (10%), with the middle lamella showing high levels of reaction at WPG's in excess of 25% (Rowell *et al.*, 1994; Hill *et al.*, 1998). Evidence from the literature therefore shows that not all accessible OH groups are reacted at the WPG threshold where decay protection occurs.



**Figure 1: Anhydride reaction scheme**



**Figure 2: Number of OH groups substituted at different WPG's for two anhydrides**

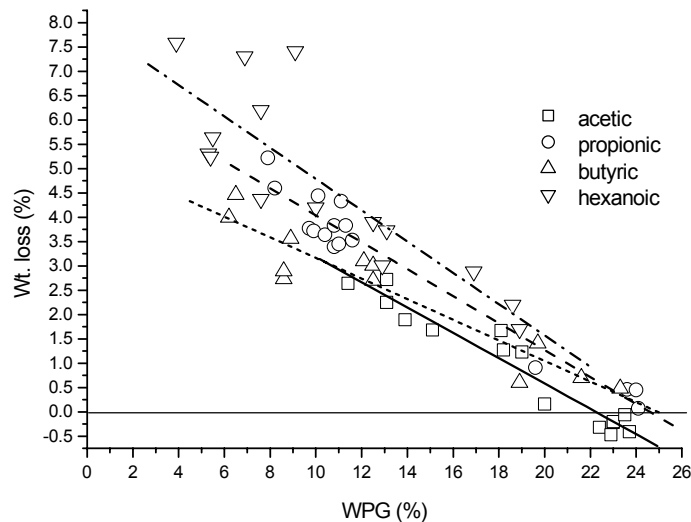
By reacting wood with carboxylic acid anhydrides of different molecular weights (Fig. 1), it is possible to achieve very different levels of hydroxyl substitution at the same WPG values (Fig. 2). Determination of the number of hydroxyl groups substituted, is determined by dividing the weight gain due to reaction per gram of oven-dry wood by the molecular weight of the adduct. Estimates of the number of accessible hydroxyl groups per gram of oven-dry wood, can also be made (Hill and Jones, 1996), to give an approximate value for the percentage of accessible OH's substituted at a given WPG (shown for 20% WPG in Table 1).

**Table 1: Number of OH groups substituted at a WPG of 20%**

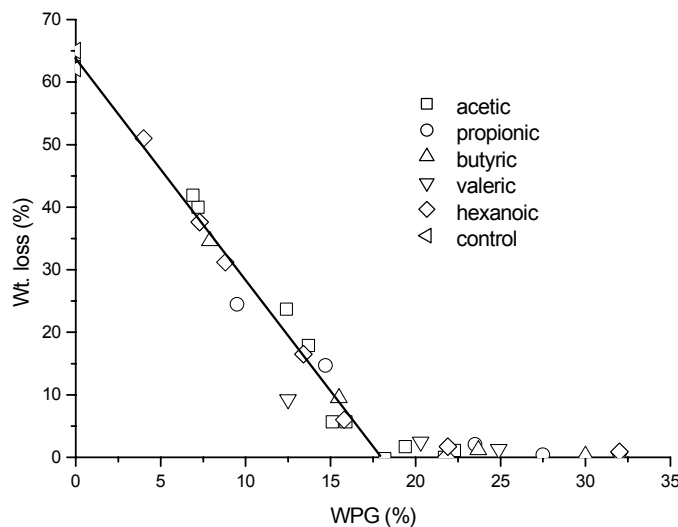
R	Anhydride	No. OH groups substituted [mmoles/g]	% accessible OH groups substd.
CH <sub>3</sub>	ACETIC	4.76	55
C <sub>2</sub> H <sub>5</sub>	PROPIONIC	3.57	42
C <sub>3</sub> H <sub>7</sub>	BUTYRIC	2.86	33
C <sub>4</sub> H <sub>9</sub>	VALERIC	2.38	28
C <sub>5</sub> H <sub>11</sub>	HEXANOIC	2.04	24

## RESULTS

Two studies have been reported where wood modified by a variety of linear chain anhydrides has been decayed by soft rot attack (Suttie *et al.*, 1999) and brown rot attack (Papadopoulos and Hill, 2002). The results for soft rot (Fig. 3) and brown rot (Fig. 4) show that WPG is the factor that determines decay resistance and not extent of OH substitution. The results in Fig. 4 also contain more recent, unpublished data from studies at Bangor.

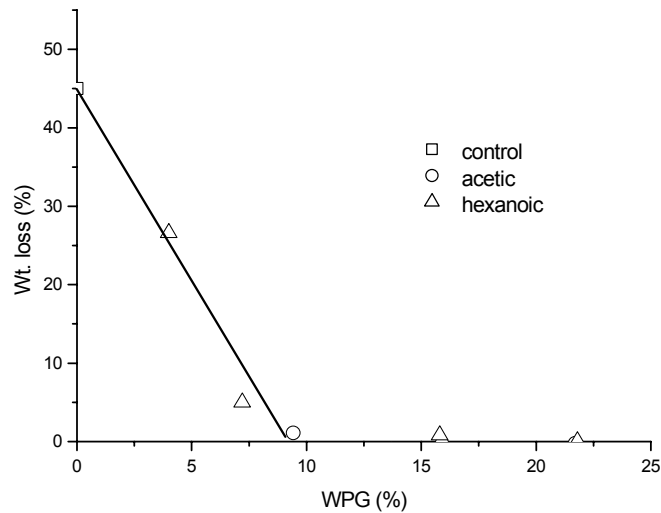


**Figure 3: Results of soft rot exposure test**

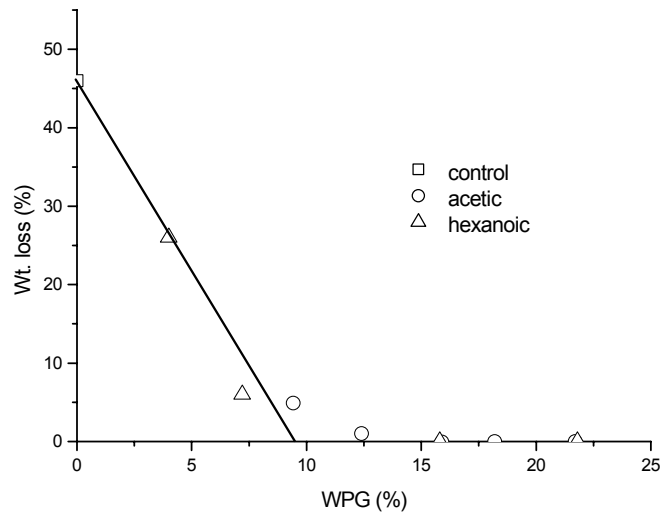


**Figure 4: Results of *Coniophora puteana* exposure tests**

The results from preliminary (unpublished) white rot decay experiments with Corsican pine sapwood modified with acetic or hexanoic anhydrides are shown below. With both the simultaneous white rot fungus (*C. versicolor*) and the preferential white rot fungus (*Phanerochaete chrysosporium*), the results indicate that decay protection is achieved at a WPG value of around 10%. This is far lower than the thresholds for soft rot, or with *C. puteana*. There is as yet insufficient data to determine whether there is any difference in efficacy between acetic and hexanoic anhydride modified wood.



**Figure 5: Results of *Coriolus versicolor* exposure tests**



**Figure 6: Results of *Phanerochaete chrysosporium* exposure tests**

## DISCUSSION

With brown rot and soft rot full protection is afforded at a WPG of around 20%, irrespective of the number of OH groups substituted. This corresponds to the point where the wood is swollen to its maximum volume by the presence of adducts in the cell wall. At a WPG of 20% there are still a considerable number of accessible OH groups that are not substituted.

With the soft rot data, at lower WPG levels, the evidence suggests that the larger anhydrides are less effective at providing protection compared to the smaller anhydrides. This indicates that degree of OH substitution is more important at lower WPG levels. There is no such evidence with the data for exposure of modified wood to *C. puteana*. It is possible that the difference in decay protection observed for soft rot at low WPG levels is related to differences in the distribution of substitution of the OH groups in the cell wall. Results from modelling of the kinetics of cell wall reactions would suggest that acetyl groups would be located in a region close to the lumen at low WPG levels, whereas with increasing size of anhydride the distribution

would become more diffusely distributed throughout the cell wall. It is postulated that a concentration of OH substitution close to the lumen surface would inhibit erosion attack or cavity formation from being initiated in this zone.

Inhibition of enzymatic function is not of primary importance in view of the fact that the enzymes cannot penetrate the cell wall of undecayed wood. The role of such enzymes in generating low molecular weight degradative agents cannot be ignored however.

The white rot data shows that the decay protection threshold is much lower than that with either soft rot or *C. puteana*. The limited data suggests that the level of substitution of OH groups is not important in view of the fact that data for acetylated and hexanoylated appears similar. The lower threshold observed with these white rot fungi may be explained if it is assumed that the phenolic OH groups of the lignin react more rapidly compared to the polysaccharide OH's. This would presumably result in the lignin being more resistant to degradation at low WPG levels. This may be due to the inhibition of the generation of phenoxy radicals in the lignin macromolecule. There is some dispute as to at what WPG level all of the lignin OH groups are substituted (or indeed whether full substitution is ever achieved). Perhaps the key point is that the *most accessible* OH groups are substituted rapidly, and that it is these that would be most susceptible to attack by degradative agents.

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## **Assessing Performance Potential of Modified Wood focussing on Dimensional Stability and Biological Durability**

Joris Van Acker

Ghent University, Laboratory of Wood Technology, Coupure links 653, 9000 Ghent, Belgium. E-mail address: joris.vanacker@rug.ac.be

**Keywords:** Testing, dimensional stability, biological durability

### **ABSTRACT**

An important objective of the Thematic Network for Wood Modification was to produce quality evaluation systems as is described under Workpackage 6 that deals with testing and standardisation.

For dimensional stability, the generally used criterion is ASE (Anti Shrinkage Efficiency). Both the test specimens, as well as the humidification cycles show considerable differences between laboratories when test methods are compared. A core standard test procedure is being proposed together with some additional methods relevant for specific performance evaluation.

Next to the prime parameter envisaged for improvement (dimensional stability) most modification systems also change the biological durability. Assessment of performance in equivalence to wood preservation can be difficult, as increased protection against fungal decay does not necessarily correspond with full decay elimination criteria. Besides this toxic value based assessment, there is a clear preference for a methodology similar to the evaluation of natural durability for different wood species. Based on a round robin test using acetylated Radiata pine this strategy is underlined. Although many other modification systems are not able to reach an efficacy similar to heavy duty preservatives, the improvements are not negligible and need to be measured in view of quality assessment.

Both the dimensional stability and the biological durability and a range of other parameters should be used as quality indicators for a commodity. The performance levels only need to be sufficient for the application envisaged.

### **INTRODUCTION**

The objectives of Work package 6 of the Thematic Network for Wood Modification are:

- To identify the areas where test specific methods and standards are required
- To produce recommended test methods to simulate in service performance, recommendations to aid in the preparation of European standards
- For some areas the preparation of drafts towards European standards should be possible

Most material properties should not be considered in an alternative way, compared to evaluating wood without modification treatment. It is inevitable for this that especially weak points of the wood modified with a special treatment need more attention than a property that is hardly influenced. It can be stated that the main goals of wood modification are linked to dimensional stability and biological durability.

### ***Durability/degradation***

Related to biological durability, two approaches could become valid standardised procedures mostly depending on the typology of the modification treatment. Though the main objective is seldom increased biological durability, wood modification can be seen as an alternative for wood preservation, or as the creation of a more durable wood species. For the former, the traditional wood preservation concept, standard testing methods like fungal tests EN 113 and ENV 807 could be applied and further implemented for authorisation through standard evaluation in line with standards like EN 599. For the second, the altered wood species properties, a natural durability evaluation could be the most sensible methodology to be used. Here CEN TC 38 WG 23 identified new standard test methods equivalent to the ones used for wood preservatives, but aiming at another concept of interpretation of the results. The efficacy of a treatment is no longer considered important, but rather the expected service life under a use class as defined in EN 335, probably in a similar way as now mentioned under EN 460. Both for the approach linked to wood preservation as the one based on natural durability there is a possibility to relate to known wood products, thereby improving the market potential. Using acetylated Radiata pine treated at SHR, a round robin test on the biological durability was set up.

### ***Dimensional stability***

Different tests methods considered by the membership of the Thematic Network for Wood Modification can be grouped as follows:

- a. dimensional change due to water soaking/impregnation
- b. dimensional change under a range of relative air humidity conditions
- c. cyclic wetting and drying
- d. altered equilibrium moisture content (EMC) and the rate to reach this point

Most methods are aimed at determining ASE (Anti Shrinkage/Swelling Efficiency) in relation to a certain WPG (Weight Percent Gain) of the treatment. Although there is major consensus on the way this should be done, some minor technical differences might still have an impact on the result. Therefore the idea of a simple round robin test using two different wood species very different in dimensional stability was launched. Based on material coming from the same origin and using the specific test conditions of the labs involved in dimensional stability testing, better insights should enable recommendations for a standard procedure. This paper already describes most parameters to be included in the methodology detailed under the experimental section.

## **EXPERIMENTAL**

### ***Round robin test biological durability***

In order to facilitate a round robin test on dimensional stability the partner SHR Timber Research (Dennis Jones / Bas Holleboom) was responsible for treatments and logistics. The partners involved in the execution of the Basidiomycetes testing were:

1. RUG Ghent University, Belgium (Joris Van Acker / Griet Plaetinck)
2. BFH, Hamburg, Germany (Andreas Rapp / Kathrin Behrmann)
3. CTBA, Bordeaux, France (Gilles Labat / Isabelle Le Bayon)
4. VTT Building and Transport, Espoo, Finland (Antti Nurmi / Leena Paajanen)
5. Dr. Wolman GmbH, Sinzheim, Germany (Joerg Habicht / Gunnar Kleist)
6. BRE, Watford, United Kingdom (Richard Thompson / Janice Carey)
7. University of Ljubljana, Slovenia (Franci Pohleven / Gregor Rep)
8. University of Göttingen, Germany (Holger Militz / Ulrich Junga)

The test wood species was *Pinus radiata* using EN 113 type blocks (15 mm x 25 mm x 50 mm), with growth ring inclination of approximately 45°. A first set (treatment 0) consisted of wood only conditioned at 65 % RH and 20°C without further treatment, while treatment 1 was dried at 103°C and as such treated to 0% WPG (Weight Percent Gain of acetylation). The treatments 2 up to 5 were acetylated at 5, 10, 15 and 20 % WPG respectively. All treated specimens (treatments 1 to 5) were leached according to EN 84.

Each set contained 2 sub-sets for the two 2 Basidiomycete test fungi used. Some additional treated Radiata pine specimens were included to verify weight changes related to conditioning, leaching and exposure without the presence of fungi. Scots pine sapwood controls were also included, both to verify fungal decay potential in each test vessel and as controls for the fungal virulence check.

Testing was executed according to EN 113 methodology in order to verify the assessment system as indicated in EN 599 for wood preservatives. Inherent to the nature of wood modification natural durability assessment is a fair assessment system too.

In order to maximise comparison and interpretation potential of the round robin experiment, the document N34 of CEN/TC 38/ WG 23 was used as guideline. This method is specifically designed to assign a biological durability level to solid wood and is not solely based on preservative concentration levels inducing mass loss percentages lower than 3%.

In order to put the biological durability testing in perspective, the following paragraphs are included to detail the content of the natural durability test methods and to provide guidance for further standardisation of test procedures used when evaluating modified wood.

The procedures as described by CEN/TC 38/WG 23 under test methods for determining the natural durability of solid wood against wood-destroying fungi consist of two parts. In part 1 Basidiomycetes (document N34) a method of test is described for determining the natural durability of a timber against wood-destroying basidiomycetes cultured on an agar medium. This method may be used in conjunction with an ageing procedure, for example EN 73 or EN 84.

Specimens prepared from the timber under test and reference timber specimens are exposed to attack by pure cultures of wood-destroying basidiomycete fungi. After a prescribed period of incubation under defined conditions, the percentage loss in dry mass of the specimens is used to estimate the resistance of the test timber to attack by the test fungi and as the basis of a provisional durability rating.

The reference timbers species are Scots pine (*Pinus sylvestris* Linnaeus) for tests with softwoods and beech (*Fagus sylvatica* Linnaeus) for tests with hardwoods. The overall obligatory test in all cases is *Coniophora puteana* (Schumacher ex Fries) Karsten (BAM Ebw. 15) (virulence check using loss in mass of Scots pine sapwood or beech in 16 weeks of minimum 30 % (m/m)). *Poria placenta* (Fries) Cooke sensu J. Eriksson (FPRL 280) should be included for softwoods and *Coriolus versicolor* (Linnaeus) Quélet for hardwoods. Both these latter fungi should have a virulence leading to a loss in mass of Scots pine sapwood or beech respectively of minimum 20 % (m/m) in 16 weeks to validate the testing.

The dimensions of each test timber specimen at  $(12 \pm 2)$  % (m/m) moisture content shall be  $(50 \pm 0,5)$  mm x  $(25 \pm 0,5)$  mm x  $(15 \pm 0,5)$  mm. The nominal volume of each specimen used for

calculation is then  $18,75 \text{ cm}^3$ . Next to test specimens, moisture content specimens are also present, which are used to establish the moisture content of the timber following conditioning to constant mass, to allow calculation of the initial dry mass of the test specimens. After conditioning, the moisture content specimens are oven dried and weighed to the nearest 0,01 g to determine the initial dry mass ( $m_0$ ). The mean moisture content ( $m_1$ ) of the moisture content specimens is then used to calculate the initial dry mass ( $m_0$ ) of each test timber specimen.

The actual exposure to fungi takes place as soon as the mycelium completely covers the surface of the culture medium starting by introducing into each culture vessel one or two test specimens introduced aseptically. The test specimens are placed on the previously sterilised support. When testing natural durability, only the timber under test is considered, while for preservative efficacy testing (EN 113) the treated specimens are each introduced alongside a control specimen of the same wood species as the virulence controls. After introducing the test specimens, the culture vessels are returned to the culture chamber (incubator or dark room controlled at  $(22 \pm 2) \text{ }^\circ\text{C}$  and  $(70 \pm 5) \%$  relative humidity) and left there for 16 weeks. At the end of the test, the specimens are withdrawn from the vessels, also removing any adhering mycelium. Evidence of waterlogging or contaminating micro-organisms is recorded in order to be able to eliminate non valid data. Each specimen is weighed to the nearest 0.01 g at the end of the test after being oven dried at  $(103 \pm 2) \text{ }^\circ\text{C}$  until the specimens have reached constant mass ( $m_2$ ). The loss in mass of each specimen is calculated by expressing the loss in mass ( $m_0 - m_3$ ) as a percentage of the initial dry mass ( $m_0$ ).

The median value is determined for the losses in mass of the test timber specimens exposed to each test fungus. The sample of timber tested shall be given a durability rating against wood-destroying basidiomycete fungi, based on the higher median mass loss determined for all the test specimens exposed to each of the two test fungi, using the scale given in Table 1.

**Table 1: Durability rating scale according to Document N34 of CEN TC 38 WG 23**

Durability class	Description	Mass Loss [%]
1	Very durable	$\leq 5$
2	Durable	$>5$ to $\leq 10$
3	Moderately durable	$>10$ to $\leq 15$
4	Slightly durable	$>15$ to $\leq 30$
5	Not durable	$>30$

There is also a test method for soft rotting micro-fungi (Part 2 or document N35 of CEN/TC 38/WG 23), which was not used in the round robin test set up but is however of importance when applications in ground contact are envisaged. The principles of this test method are summarised in the following paragraphs.

The same reference wood species are used. However, the test specimens are now mini-stakes having dimensions of  $(100 \pm 1) \text{ mm} \times (10 \pm 0,1) \text{ mm} \times (5 \pm 0,1) \text{ mm}$ . The test procedure uses natural top soil or a fertile loam-based horticultural soil of pH 6 to pH 8 with a water holding capacity (WHC) of between 25 % ( $m/m$ ) and 60 % ( $m/m$ ). Soil is deposited in a test container providing at least 120 mm depth of soil. Water is added to the soil in order to reach 95 % of its WHC. The test specimens are planted vertically with 20 mm of their length protruding above the surface of the soil.

The duration of the test needs to be verified for this procedure. When testing hardwoods, the reference timber specimens (beech) need to show a mass loss that exceeds 20 % ( $m/m$ ) to

terminate the test, while for softwoods the mean loss in MOE for each specimen (Scots pine sapwood), expressed as a percentage of the initial MOE should exceeds 40 %. The MOE is measured using a static bending test on test timber specimens after impregnation with water using the method described in EN 84 and leave the specimens in the water for 2 hours.

At the end of test the test specimens are withdrawn from the vessels and the oven dry mass for all wood species is determined supplemented by the loss in MOE for each softwood specimen (expressed as a percentage of the initial MOE).

The median loss in MOE and the median mass loss is then calculated both for the test timber specimens and for the reference timber specimens.

The median values are then used to calculate the 'x value' for the test timber specimens.

$$x = \frac{\text{median value for test timber specimens}}{\text{median value for reference timber specimens}}$$

The sample of timber tested shall be given a durability rating against soft rotting micro-fungi and other soil inhabiting micro-organisms, based on the 'x value' using the scale given in Table 2.

**Table 2: Durability rating scale according to Document N35 of CEN TC 38 WG 23**

Durability class	Description	x value
1	Very durable	≤ 0.10
2	Durable	>0.10 to ≤ 0.20
3	Moderately durable	>0.20 to ≤ 0.45
4	Slightly durable	>0.45 to ≤ 0.80
5	Not durable	>0.80

The latter rating is valid for in ground contact applications (hazard or use class 4 according to EN 335). The Basidiomycete testing and rating according to table 1 are also required for these applications but also for exterior end uses out of ground contact (hazard or use class 3).

### ***Dimensional stabilisation of timber***

The methodology detailed under this heading is giving an overview of methods as communicated on by the member of the Thematic Network for Wood Modification. The laboratory methods used for screening and scaling up at SHR Timber Research in the Netherlands are the basis for this compilation test methodology.

For testing dimensional stability most test labs prefer to use the same reference wood species as for biological testing. Scots pine sapwood (*Pinus sylvestris*) is considered to be the key material, while beech (*Fagus sylvatica*) is used if also a hardwood species is to be evaluated. Specimens differ depending on test set up, but are commonly cut from small beams with a cross section of minimum 20 mm x 20 mm up to 40 mm x 40 mm. The slices generally have a longitudinal or axial dimension of 5 up to 10 mm. The wood should be free of defects and specimens should be cut with sides fully perpendicular and parallel to the growth rings.

Preferably, matched specimens are used for the different testing procedures (adsorption, desorption, soaking) to avoid long consecutive testing with the same specimens. A minimum amount of 5 replicates is used. One of the alternative specimen sizes used are cubes, commonly 10 x 10 x 10 (up to 50) mm, with growth ring orientation (Stamm 1964). Generally the number of replicates used here is set at 10.

### **Oven drying – soaking with water**

Half of the specimens are oven dried ( $103 \pm 2$  °C). To avoid disruption of the specimens the temperature should be raised cautiously. The other half of the matched specimens is saturated with water by submerging them in demineralised water and applying a 30 minutes vacuum. This impregnation should induce specimens to sink. Ultrasonics can be used additionally to remove trapped air. After impregnation, specimens should remain in the water for at least 16 hours to guarantee a complete saturation. All specimens are weighed and subsequently tangential and radial dimensions should be determined.

At the University of Bangor, Corsican pine sapwood 20mm x 20mm x 5mm (radial x tangential x longitudinal, growth rings are parallel to the tangential face) are cut from kiln dried wood. And after treatment the blocks are vacuum impregnated with deionised water for water-soak tests. It is observed that the specimens can require up to six impregnation cycles before sample saturation. The specimens are soaked for a total of five days before determination of the water-saturated volume. Following measurement, blocks are transferred to an oven set at 105°C for a total of 72 hours in order to ensure dryness to constant weight. Once fully dry, samples are again measured and re-weighed. This procedure is repeated for a total of ten oven-dry (OD) water-soak (WS) cycles. This procedure is especially efficient to determine the ‘chemical’ stability of the chemical bonding by modification processes.

### **Conditioning**

For adsorption, previously oven dried specimens can be conditioned consecutively at *e.g.* 22%, 33%, 65%, 81% and 91% relative air humidity at 20 °C. These steps can be considered sufficient to obtain a hysteresis adsorption curve for the material under test. Critical is that the specimens are conditioned to constant weight at each step. A minimum of 7 days is always required and equilibrium should be checked *e.g.* up to maximum 0.01 g changes at 24 hour intervals. Usually up to 4 weeks are needed to be sure that equilibrium is achieved.

For desorption, saturated specimens are consecutively dried and conditioned at 91%, 81%, 65%, 33% and 22% relative air humidity at 20 °C. Weight recordings should be done at 0.01 g precision maximum 5 minutes after taking the specimens from the conditioning cabinet.

Radial and tangential dimensions need to be measured under the same conditions with a precision of 0.001 mm at mid points of each side using preferably a height gauge. When using a sliding calliper care should be taken to work with an inclined positioning of the measuring device.

Sometimes the specimens are used in a simplified cyclic procedure of conditioning *e.g.* 65% RH, 32% RH, oven dried (24h at 103°C), 32% RH, 65% RH, 86% RH, wet (impregnation with water after 1 h vacuum at 40 mbar subsequent with 24 h water storage), 86% RH, and 65% RH.

During conditioning, the specimens are stored in a temperature regulated room at 20 °C with a small fan guaranteeing sufficient air. The 65 % RH of the climatic room can be supplemented easily using an aquarium with a saturated salt solution of calcium chloride ( $\text{CaCl}_2 \times 6 \text{H}_2\text{O}$ ) for 32% RH and potassium chloride (KCl) for 86% RH. The use of static conditioning equipment (air humidity regulated above water at the corresponding dew point temperature) allows the use of other regimes like 30%, 60% and 90% relative air humidity.

**Calculations**

Based on the weight of the specimens, the *EMC* (Equilibrium Moisture Content) at each conditioning stage can be calculated for each relative humidity (RH) according to:

$$EMC_i = \frac{m_{ci} - m_{od}}{m_{od}} \quad (1)$$

with:

$EMC_i$ : equilibrium moisture content of the wood at RH  $i$ . This value is often presented as a percentage.

$m_{ci}$ : mass of the sample after conditioning at climate  $i$

$m_{od}$ : mass of the oven dry wood

For the *EMC* and all other parameters described hereafter, calculations are made for each individual specimen before determining average values. The altered *EMC* values can also be used to calculate the *MEE* (Moisture Excluding Efficiency).

Linear swelling or shrinkage for different ranges of the RH-scale can be calculated if using only swelling coefficients as determined starting from oven dry situation or shrinkage coefficients from water saturated dimensions. Based on the measured dimensions both *radial and tangential swelling or shrinkage* of the wood can be calculated:

$$S_{swell, j} = \frac{d_j - d_{od}}{d_{od}} \quad (2)$$

$$S_{shrink, j} = \frac{d_{sat} - d_j}{d_{sat}} \quad (3)$$

with:

$S_{swell, j}$ : swelling of the wood at *EMC*  $j$ . This value is often presented as a percentage and is also called "swelling coefficient"

$S_{shrink, j}$ : shrinkage of the wood at *EMC*  $j$ . This value is often presented as a percentage and is also called "shrinkage coefficient".

$d_j$ : dimension of the sample at *EMC*  $j$  (radial or tangential – this should be added to the presentation e.g.  $S_{swell, rad, 60}$  = radial swelling of the wood from oven dry to 60% RH)

$d_{od}$ : dimension of the sample after oven drying

$d_{sat}$ : dimension of the specimen after water saturation.



The volumetric swelling coefficients should first be calculated in order to determine the *volumetric ASE*:

$$S_{vol,i-j} = [(1+S_{rad,i-j})*(1+S_{tan,i-j}) - 1] \quad (4)$$

$$S_{vol,i-j} = [1 - (1-S_{rad,i-j})*(1-S_{tan,i-j})] \quad (5)$$

with:

$S_{vol,i-j}$ : Volumetric swelling (4) or shrinkage (5) coefficient from a relative humidity (RH) of i% to j%. This value is usually indicated as a percentage.

$S_{tan,i-j}$ : Tangential swelling or shrinkage coefficient (expressed as 0.0x and not as a percentage) from a relative humidity scale of i% to j%.

$S_{rad,i-j}$ : Radial swelling or shrinkage coefficient (expressed as 0.0x and not as a percentage) from a relative humidity scale of i% to j%.

The actual longitudinal swelling is not taken into account because it is negligible compared to radial or tangential swelling.

The volumetric ASE is then calculated according to:

$$ASE_{vol,i-j} = \frac{S_{vol,ref,i-j} - S_{vol,treat,i-j}}{S_{vol,ref,i-j}} \quad (6)$$

with:

$ASE_{vol,i-j}$ : Volumetric anti swelling or shrinkage coefficient as a percentage from a relative humidity (RH) of i% to j%.

$S_{vol,ref,i-j}$ : Average volumetric swelling or shrinkage coefficient of untreated (reference) samples from a RH of i% to j%.

$S_{vol,treat,i-j}$ : Average volumetric swelling or shrinkage coefficient of treated samples from a RH of i% to j%.

The ASE should be determined both radial and tangential for at least the following RH's:

- 0% RH to water saturated (complete swelling)
- water saturated to oven dry (complete shrinkage)

Equally the *linear ASE for swelling or shrinkage* can be determined. Optionally the linear ASE (*e.g. tangential or radial*) can also be determined for other parts of the RH scale.

An alternative way to calculate ASE values is based on surface shrinkage (Stamm 1964):

$$S = \frac{A_s - A_{od}}{A_{od}} \quad (7)$$

with

S = swelling coefficient

$A_s$  = surface of the wet specimen [mm<sup>2</sup>]

$A_{od}$  = surface of the oven dried specimens [mm<sup>2</sup>]

This volumetric ASE calculation uses swelling or shrinkage of volumes calculated at each stage. Since the longitudinal dimension is not taken into account a volume value at each stage can be replaced by a multiplication of the radial and tangential dimensions (surface A).

### **Minimal full evaluation**

A simplified version identifies only a multiple soaking-drying ageing test (e.g. 3 cycles), where each cycle consists of a vacuum impregnation with distilled water, immersion overnight and subsequent drying at  $103 \pm 2^\circ\text{C}$  for 24 hours. A conditioning at different air humidities can be added using specimens consecutively conditioned for 4 weeks at 60% RH -  $20^\circ\text{C}$  (dry room conditions) and at 90% RH -  $20^\circ\text{C}$  (wet room conditions) as an indication for water vapour impact. In each case anti-shrink efficiency (ASE) is calculated based on comparison of modified and unmodified specimens.

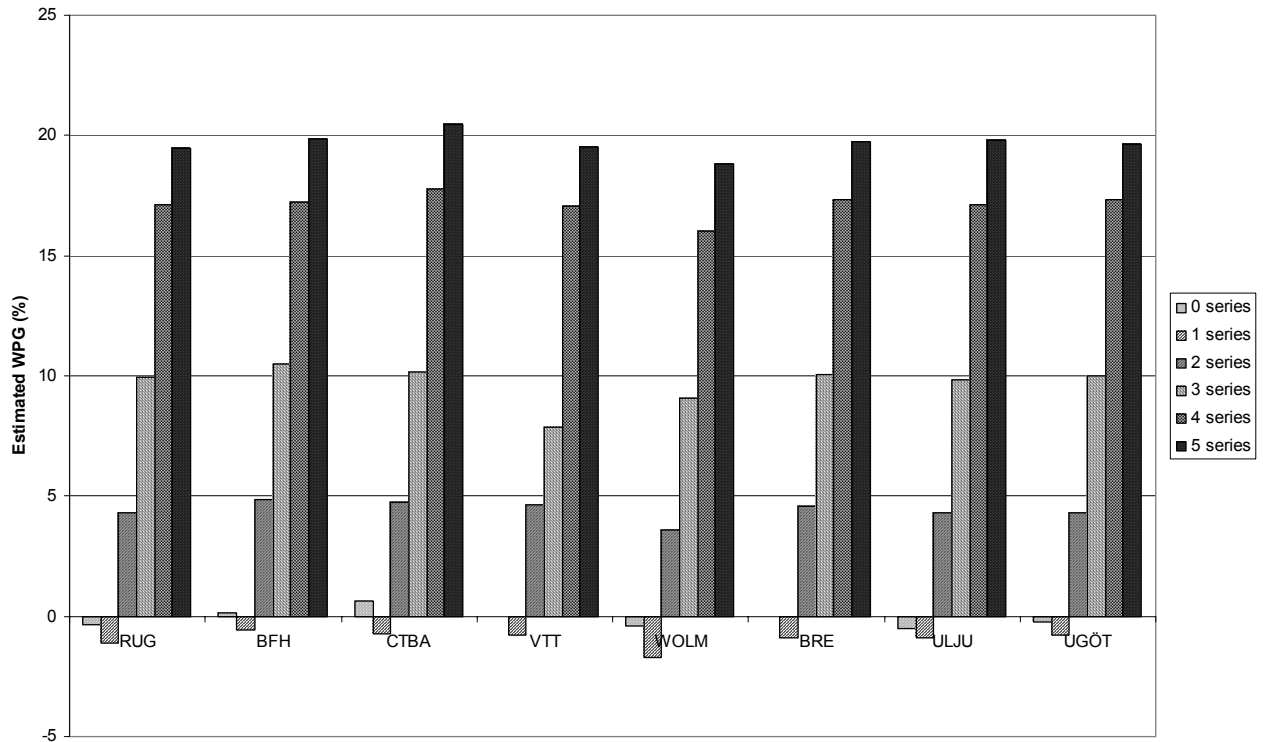
### **Round robin set up**

During the last year of the Thematic Network for Wood Modification, a simple round robin test was set up for dimensional stability evaluation. In order to allow different specimens sizes to be used and to guarantee the same reference material tested, it was considered incorrect to start from a modification treatment applied to beams. Avoiding an uneven modification would be impossible. This was solved by selecting two hardwood species with major differences in dimensional stability: the reference wood species beech (*Fagus sylvatica*) and so-called 'treated beech' being afzelia (*Afzelia bipendensis*).

## **RESULTS**

### ***Round robin test biological durability***

Based on the correction factor calculation in a fungal test set up as defined by EN 113 it is possible to calculate the WPG retained after all steps have been performed: modification, leaching and presence in fungal test vessels for 16 weeks without presence of a fungus. These data summarised for the different test institutes in figure 1 correspond very well with the treatment levels since treatments 2 up to 5 were acetylated at 5, 10, 15 and 20 % WPG respectively, while series 0 was only conditioned and series 1 was oven dried and leached, not acetylated. The latter shows that some impact of these parameters is present, since the losses of series 2 are significant compared to series 1. These negative values correspond in fact with small amounts of WPG not included in the estimated values for the acetylation treatments 2 to 5. The small differences in acetylation degree between the materials used for testing in the different test labs (e.g. at VTT and Wolman) can be used for further interpretation but should be of minor importance.



**Figure 1: Estimated WPG (weight percent gain) based on blocks free of fungal exposure**

The fungal test results with *Coniophora puteana* are detailed in figure 2. Both mean and median mass losses for each treatment are given, in order to visualise variability and to allow interpretation according to EN 113 (wood preservative efficacy) and CEN TC 38 WG 23 document N34 (natural durability) respectively (Van Acker *et al.* 20003).

All results up to 10 % WPG (treatment 3) show mass losses of over 20 %. Although significant differences in mass loss can be observed for these lower degrees of acetylation, a fairly high degree of uniformity can be observed, taking into account that no fungal strains were exchanged for this round robin test and that laboratory practices were only standardised under the constraints of the procedures as described in the standards. Based on the rating scale as defined in table 1 all this material should be considered not durable up to slightly durable. For treatment 4, actually at approximately 17 % WPG, the results do differ between test institutes. At Wolman (WOLM) this concentration is already situated above the toxic limit (below 3 % mass loss) while at RUG the material can be classified as very durable according to table 1. At BFH and CTBA the same treating level allows classification as durable, whilst only moderately durable based on the results from BRE. The mass losses recorded at the other institutes are on the borderline between moderately and slightly durable wood (15 % mass loss). Both at CTBA and the University of Ljubljana (ULJU) the 20 % WPG was not sufficient to stop fungal decay by *Coniophora*, while the other 6 labs observed mass losses below 3 %.

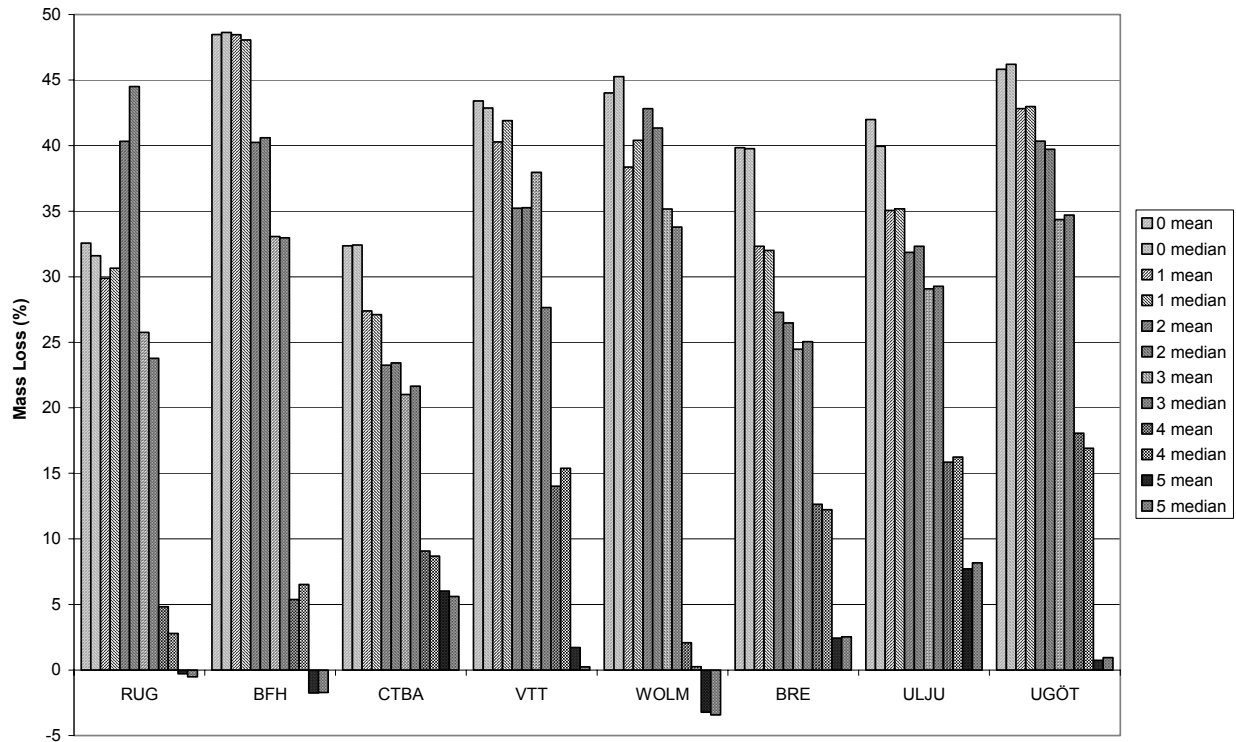


Figure 2: Mean and median mass losses by *Coniophora puteana* for treatments 0 to 5

The results with *Poria placenta* are given in figure 3. Although this fungus does not always attain a 20% mass loss for untreated radiate pine, the ability to prevent decay of this fungus by acetylation is not necessarily achieved at lower retention levels than *Coniophora puteana*.

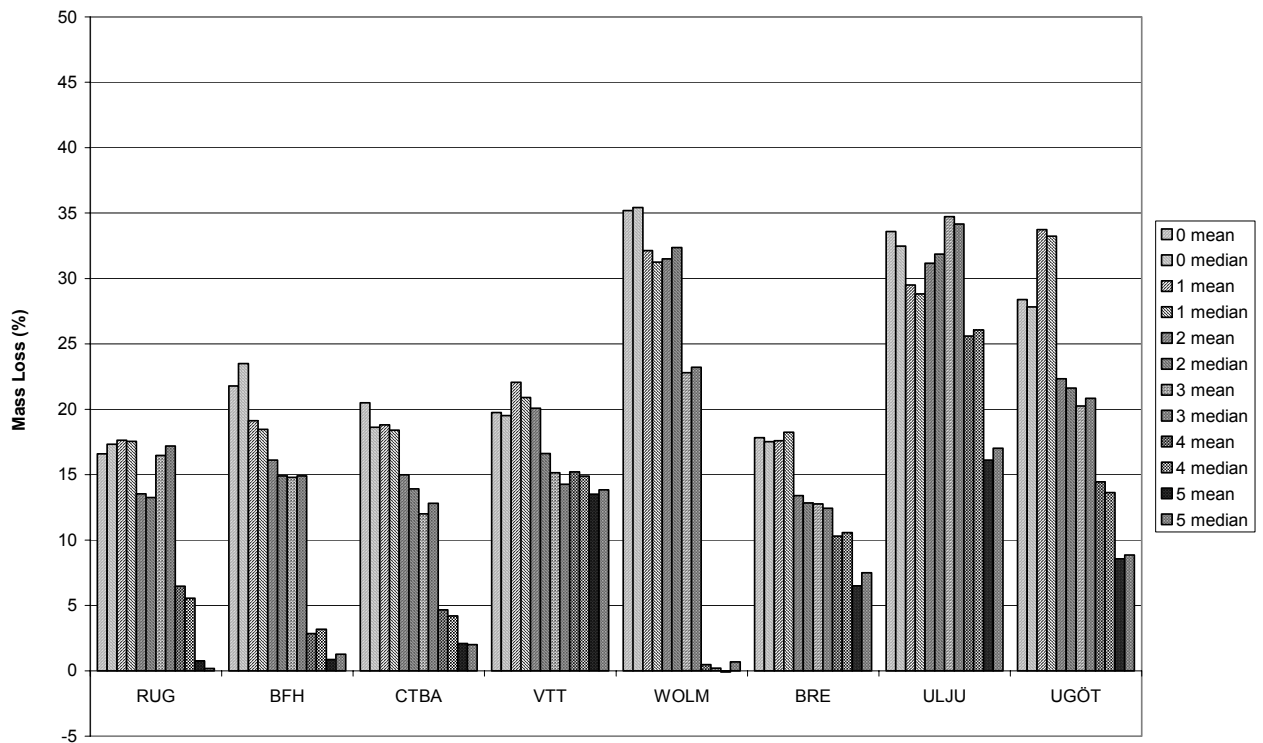


Figure 3: Mean and median mass losses by *Poria placenta* for treatments 0 to 5

High mass losses for control material are however not linked to high decay rates at higher acetylation degrees as can be observed when comparing results from CTBA and the University of Ljubljana (ULJU). For biological durability classification, according to table 1 of the acetylation levels up to 10 % (treatment 3), the results obtained with the fungus *Poria placenta* are not decisive as the highest median mass losses were obtained with *Coniophora puteana* (Fig. 1). The classification of moderately durable up to slightly durable for treatment 4, as observed with *Coniophora* at BRE, VTT and the Universities of Ljubljana and Göttingen (ULJU and UGÖT) seems only altered at the University of Ljubljana. However, also here the classification remains at slightly durable since this class corresponds with mass loss from 15% up to 30 %. For these four test institutes the mass losses are not considerably lower when the acetylation degree is raised from 17 to 20 %. Only at BRE and the University of Göttingen the material can be classified now only as durable (5 to 10 % mass loss). Toxic limit values are obtained in a very similar way at RUG, BFH and CTBA at 20 % WPG, while already at 17% acetylation this can be derived from the results at Woman.

It could be that differences in virulence as observed to a certain extent for control specimens of radiate pine are important to explain some of the differences reported here. Therefore details are given on the mass losses observed with Scots pine sapwood virulence controls.

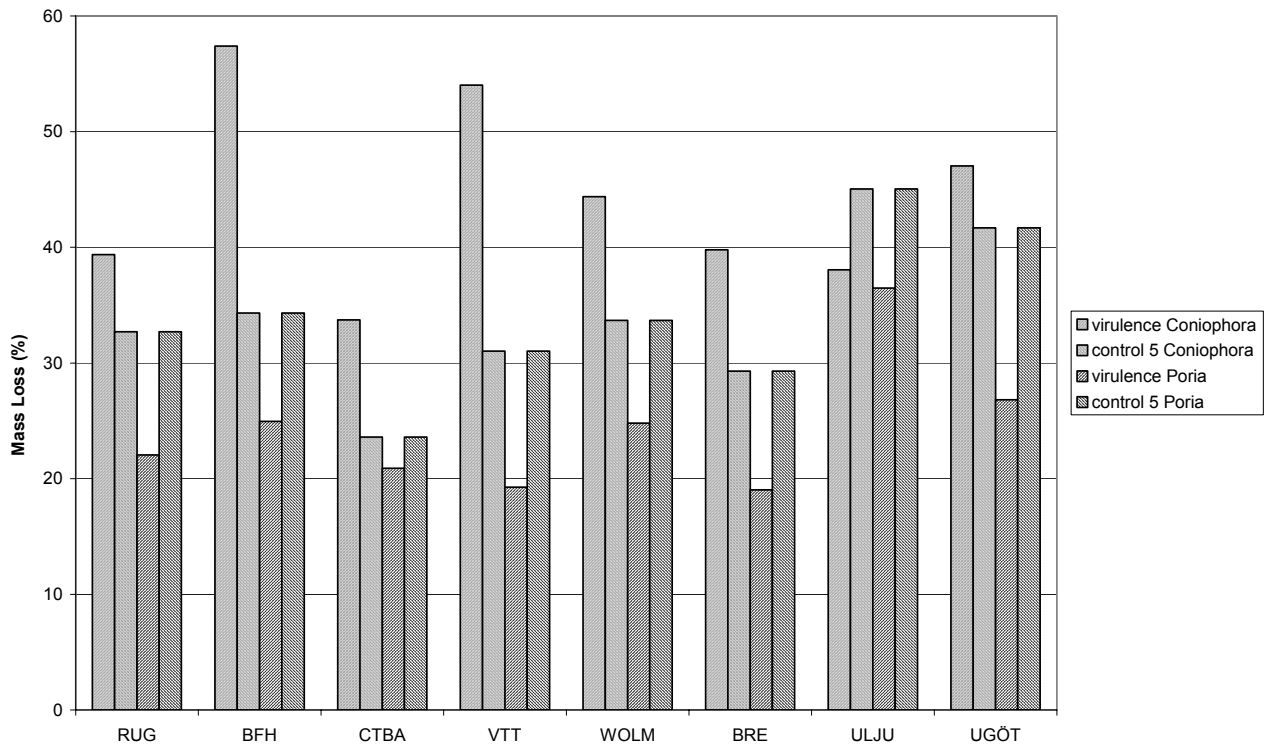


Figure 4: Virulence of *Coniophora puteana* and *Poria placenta*

The actual virulence specimens are exposed in fungal culture vessel separately, while specific test control specimens are combined in each vessel with each treated radiate pine specimen under test. The mass losses as recorded for virulence controls are nearly all above the critical level of 20 % (slight deviation for *Poria* at VTT and BRE) enabling to validate the tests according to EN 113 (Fig. 4). For validation according to the natural durability test methodology (CEN TC 38 WG 23 document N34) as detailed under the experimental, a 30 % mass loss is required for virulence control of *Coniophora*, and this criterion is also met. The higher virulence of *Coniophora* on control specimens e.g. at BFH and VTT seems not to correspond with the highest mass losses of wood acetylated at 20 % WPG (Fig. 2). The lower virulence observed at CTBA

was actually inducing the second highest mass losses for the highest acetylation level tested. For the data recorded at the University of Ljubljana, a link between high virulence and mass loss of highly acetylated wood could be valid. Here it is interesting to observe that specific control specimens incorporated alongside acetylated specimens at 20 % WPG (control 5 Coniophora) showed higher mass losses, which could be interpreted as stimulation by the presence of acetylated wood. *Poria placenta* is in this respect stimulated at all test institutes. The mass losses recorded for the control Scots pine sapwood blocks placed besides radiate pine 20 % acetylated (control 5 *Poria*), are always significantly higher than the mass losses recorded for the real Scots pine virulence controls. The highest virulence of *Poria* recorded at ULJU corresponds with the highest mass losses recorded (Fig. 3), but this is not a general relationship, e.g. when observing data from VTT.

### ***Dimensional stabilisation of timber***

Different properties of dimensional stability are related to specimen dimensions and how ASE values are calculated. Several institutes participated in a round robin test on dimensional stability. Partial results from two partners are given in this paper. The results from Ghent University (Joris Van Acker / Pascal Urbain) presented here focus on the different ASE values derived depending on type of dimensions taken into account and quality of the specimens used. In table 2 results are given for swelling from oven dry up to water saturated status. The reference wood species is beech while for the stabilised or treated wood is the wood species afzelia is used as a comparison material. Swelling coefficients are given for radial, tangential and volume (surface) dimensions. Two sets of each 10 replicates were evaluated. The first set consisted only of specimens with 40 mm sides perfect parallel to radial or tangential planes (//) while the second set deviate up to 30° from this ( $\pm$  //). The mean volumetric ASE (Anti Swelling Efficiency) values obtained for the perfect specimens is 75 %, while 77 % and 69 % are derived for tangential and radial dimensions respectively. These values are substantially lower for non perfect specimens especially for the radial direction (only 37 %).

**Table 2: Results on swelling from oven dry up to water saturated status**

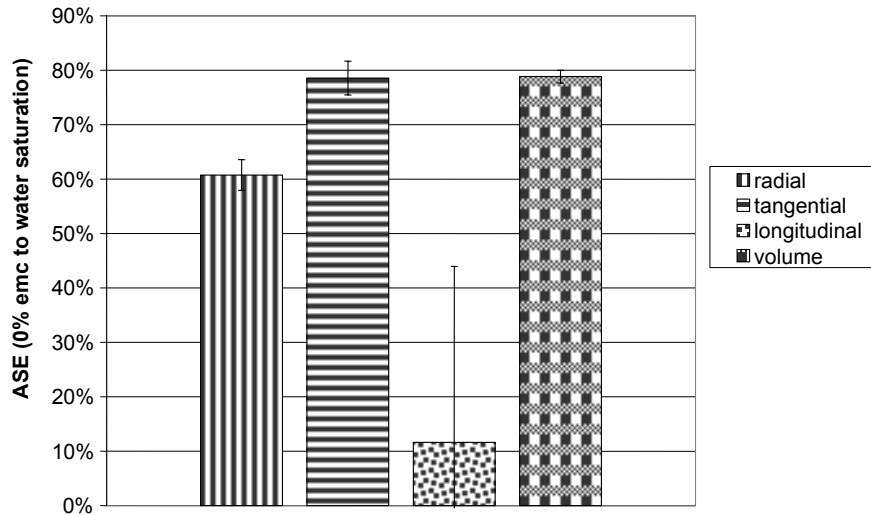
Specimen	S <sub>swell,tan</sub> [%]	S <sub>swell,rad</sub> [%]	S <sub>swell,vol</sub> [%]	ASE <sub>tan</sub> [%]	ASE <sub>rad</sub> [%]	ASE <sub>vol</sub> [%]
Reference //	14.3	6.2	21.3			
Stabilised //	3.2	1.9	5.2	77	69	75
Reference $\pm$ //	15.0	6.4	22.3			
Stabilised $\pm$ //	4.7	4.0	8.9	68	37	60

After water saturation, the specimens were dried again and analogous shrinkage values were calculated. Stability of afzelia (stabilised 'beech') is somewhat lower after water saturation which includes leaching anyway. The mean volumetric ASE (Anti Shrinkage Efficiency) obtained for the perfect specimens is 66 % and the tangential and radial ASE are 74 % and 42 % respectively. Even more substantial deviations from these values were derived for the non perfect specimens.

**Table 3: Results on shrinkage from water saturated up to oven dry status**

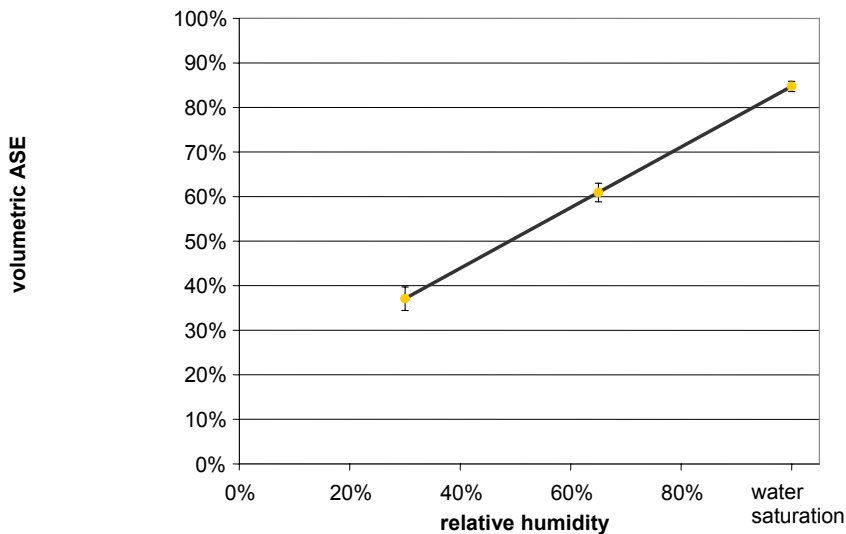
Specimen	S <sub>shrink,tan</sub> [%]	S <sub>shrink,rad</sub> [%]	S <sub>shrink,vol</sub> [%]	ASE <sub>tan</sub> [%]	ASE <sub>rad</sub> [%]	ASE <sub>vol</sub> [%]
Reference //	12.8	3.8	16.1			
Stabilised //	3.3	2.2	5.4	74	42	66
Reference $\pm$ //	11.0	3.9	14.4			
Stabilised $\pm$ //	4.1	3.7	7.6	62	5	47

A second set of tests was conducted by the University of Göttingen (Carsten Mai / Andreas Krause) and was executed using 25 mm radial /tangential – 20 mm longitudinal blocks consecutively oven dried, conditioned in a climatic chamber at 30 % and 65 % relative humidity and then water saturated by means of impregnation with water. Results are given in figures 5 and 6. Figure 5 leads to the same conclusions as derived from the data on fully parallel specimens in Table 2.



**Figure 5: ASE in radial, tangential and longitudinal direction and volumetric ASE calculated for the range between oven dry and water saturated wood**

In figure 6 the volumetric ASE calculated for equilibrium at 30 % and 65 % relative humidity and water saturated differ from 40% to more than 80 %.



**Figure 6: Volumetric anti-swell-efficiency (ASE) calculated from radial and tangential swelling**

## DISCUSSION

### ***Round robin test on biological durability***

Although no fungal strains were redistributed, nor were there specific extra instructions given on execution of the Basidiomycete test apart from the ones given in the standards, all testing was successful in all institutes participating in the round robin test on biological durability. Nevertheless this was not translated to full uniformity of the results. The evaluation as a wood preservative as well as the natural durability approach induces different approval options for acetylation based on the results obtained in individual test institutes. Based on the data recorded for the highest acetylation level tested (20 % WPG), acetylated wood could be approved equally as a wood preservative based on the results from RUG, BFH and Wolman. Based on the mass losses recorded at CTBA, BRE and the University of Göttingen acetylated wood is comparable to a durable wood species. Especially the high decay level of *Coniophora puteana* at VTT and the University of Ljubljana brings 20 % acetylated radiate pine even to a lower durability class evaluation. As these differences are important for the industrial implementation of acetylated wood, like this acetylated radiate pine, it appears logic that the evaluation should take into account a range of parameters besides the simple biocidal efficacy (Van Acker 2001).

### ***Dimensional stabilisation of timber***

Based on the simple comparison of ASE results obtained in swelling or shrinkage, calculated based on tangential, radial or volumetric dimensions, either using perfect or not fully parallel specimens, significant different values were calculated. These variations are not even including the impact of biological variability of the wood used, nor of deformations of test specimens due to the modification processes. ASE values also differ when they are based on conditioning (equilibrium under different relative air humidities) instead of water saturated. It is therefore essential that as much as possible perfect specimens are used and ASE values are calculated the same way when treatments are compared. This is especially valid when treating parameters are optimised during the scaling up process of modification systems.

## CONCLUSIONS

The Thematic Network for Wood Modification was successful in integrating the methodology to evaluate biological durability and dimensional stability using laboratory test methods. The round robin test on biological durability proved the possibility to evaluate acetylated radiate pine both as a preservative treated wood and as a material having a 'natural' durability. The classification obtained was not consistent over the test institutes, but there is no indication that this variability would be higher compared to different results obtained for wood preservatives tested on their efficacy or wood species evaluated on their natural durability. Based on the fact that full protection against fungal decay is not always achieved, this underpins the need for an approach on prolonged service life rather than the simple wood preservative assessment. Even based on results showing significant mass losses, a substantial improved biological durability can be expected. Combined with other increased wood quality parameters, wood modification can anyway contribute to a better commodity quality in total.

Related to the methodology to measure dimensional stability, it is obvious that the range of laboratory methods is extensive although similarities like the calculation of an ASE value may lead to the assumption that data are simply comparable. The actual impact of measurements used and specimens' characteristics can influence the outcome considerably.



It is important to use both the dimensional stability and the biological durability alongside a range of other parameters as quality indicators for a commodity. However the performance levels only need to be sufficient for the application envisaged.

### ACKNOWLEDGEMENTS

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## Microwave Modification of Wood Properties

Peter Vinden and Grigori Torgovnikov

Cooperative Research Centre for Wood Innovation, University of Melbourne, Australia

**Keywords:** Torgvin, Vintorg, chemical modification, microwaves, drying, preservative treatment

### ABSTRACT

High intensity microwaves have been used to generate steam pressure in green timber. This results in the rupturing of un-lignified ray tissue and pit membranes in radiata pine, the generation of micro-voids at the ray/fibre interfaces, and the rupturing of tyloses in hardwoods. The degree of modification varies with the intensity of microwaves applied. At low levels, micro-voids are created that cannot be seen, but nevertheless have a major impact on the drying properties of the wood. In addition, there is relatively little strength loss. At very high microwave intensities, the micro-voids expand to become visible; the wood expands in cross-section and becomes very permeable and the strength properties are reduced substantially. However, the high permeability of the wood is exploited by impregnating the wood with resins and other chemical modification agents. The wood is then pressed back to its original dimensions and cured. The resulting properties include improvements in durability, dimensional stability, strength, hardness and other aesthetic characteristics. The technology appears to be suitable for hardwoods and softwoods alike.

### INTRODUCTION

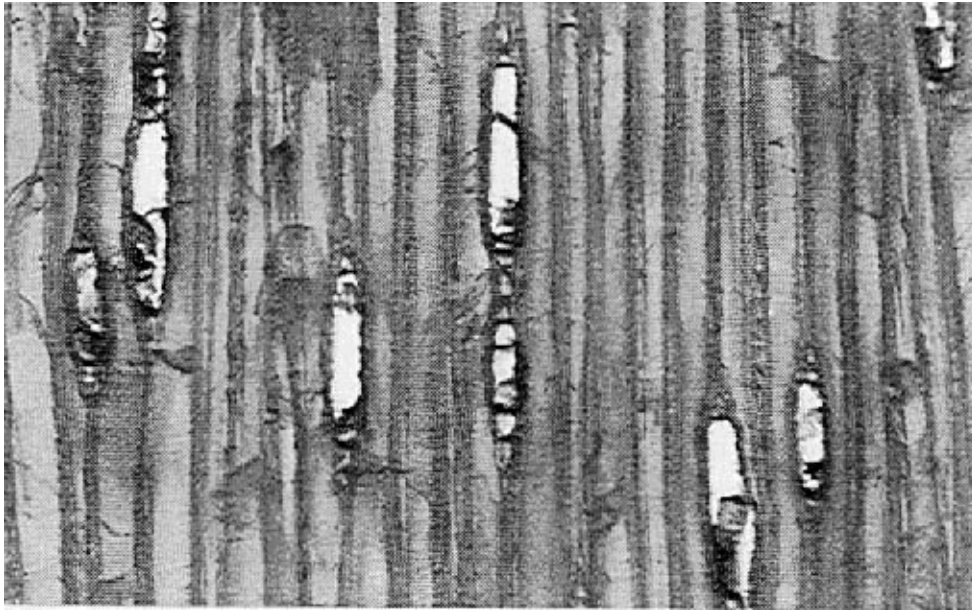
Wood permeability is a key attribute that affects all aspects of wood processing. As a general rule, wood is dried prior to impregnation with preservatives. Drying has the effect of increasing the void volume available for preservatives. Drying may also provide better macro- and micro-distribution of preservatives, and therefore better performance against biological agencies. Pressure steaming of radiata pine is unique in providing a method of conditioning that facilitates a high standard of preservative treatment at high wood moisture contents (Cobham and Vinden 1995). However, the application of pressure steaming to non-pine species has generally failed to provide any significant improvement in wood permeability or preservative treatment.

This paper describes some preliminary results obtained following the application of intensive microwaves to green wood. Microwave irradiation generates steam within the wood structure that appears capable of modifying the structure and permeability of all wood species (Vinden and Torgovnikov 1999). The intensity of microwave application also controls the extent of wood modification and its suitability for a range of processing options (Torgovnikov and Vinden 2000).

### TREATMENT OF GREEN RADIATA PINE

Steam conditioning of radiata pine (*Pinus radiata* D. Don.) green timber or round-wood under pressure (at approximately 127°C) for preservative impregnation has been used for approximately 40 years in New Zealand and Australia (McQuire 1974, Vinden and McQuire 1977, Bergervoet 1983, Vinden 1988, Cobham and Vinden 1995). The success of steam conditioning arises from the blowing out of soft radial tissue and moisture loss after steaming, and the very high standard of preservative distribution that can be achieved following pressure

impregnation. The rates of chemical penetration into steam conditioned radiata pine are spectacular, with total sapwood penetration being achieved within a few minutes of pressure impregnation (McQuire 1974). This arises from the unique structure of radiata pine and closely related pine species where the soft radial parenchyma tissue is easily ruptured, thus providing radial pathways for preservative penetration. In other pine species and most other wood species, the ray tissue is lignified and is not ruptured by steaming. Under these circumstances, pressure steam conditioning has relatively little impact on the microstructure of wood, and there is little improvement in wood permeability. Figure 1 illustrates the impact of steam conditioning on the microstructure of ray tissue in radiata pine. Radiata pine is characterised with uniseriate ray tissue that is ruptured immediately after steam conditioning.



*Figure1: Rupture of uniseriate ray tissue in radiata pine following steam conditioning*

The potential for substituting microwave irradiation for steam conditioning was investigated by Vinden and Torgovnikov (1999), Torgovnikov and Vinden (2000), Torgovnikov *et al.* (2000a) and (2000b), Vinden *et al.* (2000). The benefits of microwave processing include shorter processing times, the potential for on-line or automated treatments and a potential reduction in the strength losses associated with steaming. Pressure steam conditioning can result in strength losses to the order of 25% modulus of rupture (MOR) and 18% modulus of elasticity (MOE) (Collins and Vinden 1987). Much of the strength loss is thought to be due to the hydrolysis of cellulose. The short exposure times associated with MW processing may tend to minimise the extent of wood hydrolysis. A further potential advantage of MW conditioning includes the potential for concomitant moisture loss and structural modification. Steam conditioning requires a minimum holding period of 24 hours for alternating pressure method treatment (APM) or 7-21 days of air drying (depending on the diameter of pole and weather conditions) to achieve moisture losses that will provide an adequate treatment standard (Vinden and McQuire 1977). The results of trials to evaluate whether MW irradiation can be used to substitute for steam conditioning (Vinden *et al.* 2000) indicates that:

- MW conditioning results in the same rupturing of ray tissue as achieved with steam.
- Full treatment of 90x45 mm timber can be achieved following vacuum pressure impregnation (Bethell) once green sapwood achieves moisture contents of approximately 124% moisture content.

- Microwave conditioning could be achieved within a few minutes of irradiation.
- The total costs of MW conditioning (including capital and operating costs) are of the order of AUS\$25/m<sup>3</sup>, depending on the costs of power.
- High standards of treatment can be achieved in both sapwood and heartwood.

### TREATMENT OF REFRACTORY HARDWOODS

Whilst steam conditioning is ineffective as a means of improving the permeability of many refractory softwoods and hardwoods, microwave conditioning has been used successfully to improve both the treatability and drying of hardwoods (Vinden and Torgovnikov 2000) *etc.*

Love *et al.* (2001) had undertaken a more detailed investigation of the influence of microwave irradiation on the permeability of *Eucalyptus globulus* heartwood. The objective was to quantify changes in wood permeability measured in the radial, tangential and longitudinal directions of wood following microwave modification. The MW schedules are defined in table 1.

*Table 1: Microwave treatment schedules.*

	Sample Size=15x15mm		Sample Size=25x25mm	
Output power=4 kW	Speeds	Residence time	Speeds	Residence time
	0.8 cm s <sup>-1</sup> 1.2 cm s <sup>-1</sup>	10 s 6.7 s	0.55 cm s <sup>-1</sup> 0.8 cm s <sup>-1</sup>	14.5 s 10 s
Output power=5 kW	Speeds	Residence time	Speeds	Residence time
	1.2 cm s <sup>-1</sup> 2.0 cm s <sup>-1</sup>	6.7 s 4 s	0.8 cm s <sup>-1</sup> 1.2 cm s <sup>-1</sup>	10 s 6.7 s

A 27 year-old *E. Globulus* tree grown under plantation conditions in Victoria, Australia was used for the trials. Wood permeability was measured by soaking oven-dry wood samples measuring either 15x15x15 mm, or 25x25x25 mm, in which five sides of the blocks had been sealed with an epoxy resin, leaving one side (either radial, tangential or longitudinal) free to absorb the solvent. Rates of kerosene uptake for microwave modified wood in the three grain directions are summarised in figure 1 and compared with controls in figure 2. Figure 4 illustrates the micro-voids created after MW irradiation.

There is a substantial increase in uptake of kerosene in MW irradiated samples. The highest improvement was found in the radial grain direction. Kerosene uptake follows a pattern of almost instant uptake followed by a period of slow movement of kerosene into the surrounding tissue. The increases in uptake are associated with the presence of radially orientated micro-voids created during microwave treatment. These provide a radial path of least resistance for absorbed liquids.

Generating steam pressure within the wood influences the pattern of micro-void formation. The weaker parenchyma tissue in the radial grain direction is affected preferentially. Micro-voids appear to be initiated in the radial parenchyma at fibre/ray intersections and are influenced by microwave output power, residence time and sample size. There is some evidence to suggest that the modification process also results in the fracture of tyloses. This is desirable since it would contribute to an improvement in the lateral movement of chemicals from micro-voids (Love *et al.* 2001b).

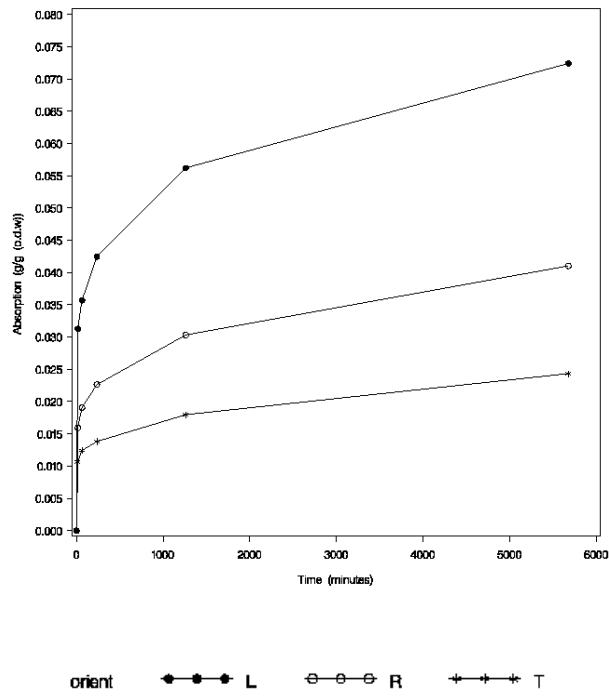


Figure 2: Absorption of kerosene in the radial, tangential and longitudinal grain directions following MW conditioning.

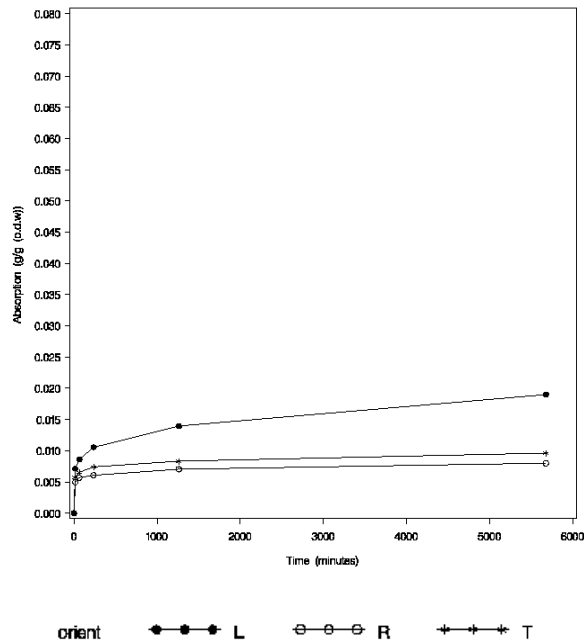
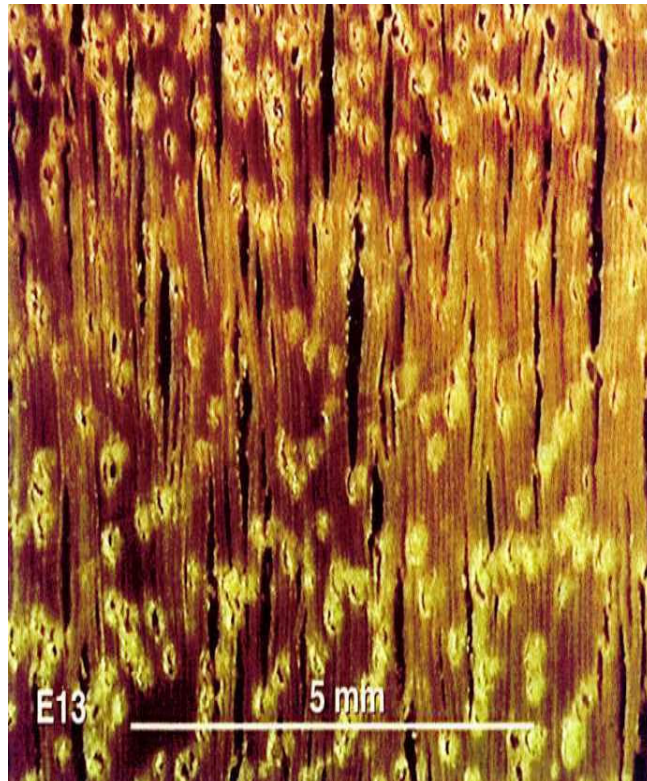
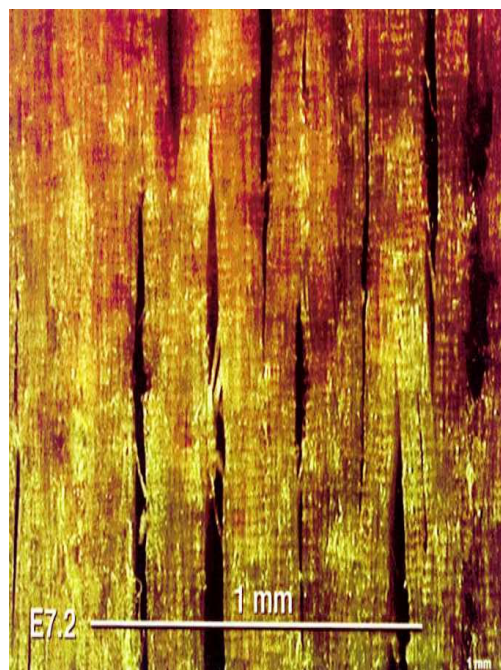


Figure 3: Absorption of kerosene in the radial, tangential and longitudinal grain directions: Control samples



*Figure 4: Creation of micro-voids in the radial-longitudinal Eucalyptus oblique*

The application of more intense MW irradiation leads to an expansion of micro-voids so that they become visible to the naked eye. There is a concomitant increase in the cross-section dimensions of the timber (Torgovnikov and Vinden 2001). The wood cross-section is 'spongy' when pressed tangentially. The appearance of *Torgvin* is illustrated in figure 5.



*Figure 5: Torgvin (intensively microwaved solid wood)*

*Vintorg* is manufactured by impregnating kiln dried *Torgvin* with resin followed by compressing the timber back to its original dimensions and curing the resin. Alternatively, the timber can be compressed back to a smaller dimension than the original cross-section to impart additional strength. The cost of *Vintorg* manufacture is influenced by the amount of resin needed to impart bonding of the micro-voids. The studies undertaken by Love *et al.* (2001) are currently being used to design treatment schedules to maximise the penetration of micro-voids whilst minimising absorption into the woody tissue.

Figure 6 illustrates a cross-section of *Vintorg* that has been impregnated with a low viscosity formaldehyde based resin. The resin was applied by soaking for five minutes. It has penetrated the total cross-section *via* the micro-voids created by microwave modification. Some lateral movement of the resin has occurred prior to pressing and curing. To some extent, it may be possible to manipulate the aesthetic characteristics of *Vintorg* by colouring the resin and controlling its lateral movement from rays to simulate the appearance of alternative wood species. The aesthetic character of wood is greatly influenced by the width and colour of ray tissue.



**Figure 6: *Vintorg* (resin impregnated and pressed *Torgvin*)**

## CONCLUSIONS

Wood permeability influences a number of important processes associated with the drying and treatment of wood with chemicals. Microwave wood modification can be used to replace steam conditioning as a method of preparing radiata pine for preservative treatment. Microwave conditioning improves the permeability of radiata pine heartwood as well as sapwood so that one can avoid the need for segregating permeable heartwood from the less permeable (or more variable) heartwood. All tracheids in radiata pine are closely associated with ray tissue so that there is very rapid movement of chemicals from the ray tissue into the tracheids through pit pairs. The soft ray tissue in radiata pine is ruptured during microwave conditioning, whereas in most other wood species, it is anticipated that micro-voids are created at the ray/fibre intersection.

The application of very intensive microwaves leads to an expansion of micro-voids such that they become visible to the eye and there is an expansion of the wood cross-section. The permeability of such material allows very rapid flashing-off of moisture and very rapid penetration of resin simply by soaking. This allows very easy chemical modification of wood prior to pressing the timber back to its original dimensions. Clearly, much more rapid resin penetration can be achieved by using vacuum/pressure impregnation.

## ACKNOWLEDGEMENTS

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## Sorption Properties of Steam Treated Wood and Plant Fibres

Hoffmeyer, P.<sup>1</sup>, Jensen, S.K.<sup>2</sup>, Jones, D.<sup>3</sup>, Klinke, H. B.<sup>4</sup>, Felby, C.<sup>5</sup>

<sup>1</sup>Department of Civil Engineering, Technical University of Denmark

<sup>2</sup>Junckers Industries Inc., Denmark

<sup>3</sup>Building Research Establishment – Centre for Timber Technology and Construction, U.K.

<sup>4</sup>Plant Research Department, Risø National Laboratory, Denmark

<sup>5</sup>Plant Fibre Laboratory, Royal Veterinary and Agricultural University, Denmark

**Keywords:** Plant fibres, sorption, dimensional stabilisation, hygrothermal treatment

### ABSTRACT

Hygrothermal treatment of wood and plant fibres was carried out to improve the dimensional stability of the fibres and products made from these. Fibres of Norway spruce, beech, wheat and hemp were included. The efficiency of the treatment was assessed by studying the moisture sorption properties. Chemical analyses were employed to possibly explain the observed changes of sorption characteristics. The fibres were steam treated at temperatures between 140 °C and 190 °C. The duration of treatment was from 5 to 60 minutes. Conditioning was done in a high precision climate chamber allowing weighing of the fibre samples to take place without removing these from the climate chamber.

A mild treatment resulted in a reduction of sorption at all levels of relative humidity (RH), although relatively most pronounced at low levels of RH. At progressively longer durations of treatment or progressively higher temperatures the behaviour was different for low/medium RH and high RH. For low/medium range RH (< ca. 85 %) the reduction of sorption continued until a lower limit was reached corresponding to approximately 30 % reduction of moisture uptake. The reduction of sorption developed at a faster rate the lower the RH. This behaviour corresponds to the reduction of the number of primary sorption sites on *e.g.* hemicellulose. For high range RH (> ca. 85 %) two additional mechanisms may have been active. One is the capillary sorption in micropores created as a result of the thermal degradation of cell wall matter. A second mechanism may be the gradual filling of such micropores by lignin made to flow by further steam treatment. As a result of these counteractive mechanisms, sorption at high RH in steam treated fibres was seen to first grow, then drop and ultimately settle at a level corresponding to pure sorption at primary sorption sites.

The annual plant fibres proved less susceptible than wood fibres to chemical breakdown from steam treatment. The component most susceptible to chemical breakdown was hemicellulose. Beech, wheat and hemp showed only a modest decrease of cellulose content, even at high temperatures, whereas spruce, surprisingly, exhibited a marked breakdown of cellulose. The latter may be correlated with the structure of softwood lignin.

### INTRODUCTION

The use of steam and pressure has long been recognized as a method to improve the dimensional stability of wood and plant fibres. Such treatments may have the primary objective of improving dimensional stability and be carried out *e.g.* as pre-treatments of raw materials for panel

products. Alternatively, conditions equivalent to hygrothermal treatments may develop in processes needed for plasticisation of wood and for curing of binders during panel production. The effects of hygrothermal treatment of wood and wood fibres are well documented (Stamm *et al.* 1946, Zhang *et al.* 1997, Sekino *et al.* 1997, Morsing 1998, Jones *et al.* 1998, Jones 1999). However, the effects of such treatment of annual plant fibres such as wheat and hemp are lesser known. At the same time such fibres are used increasingly as raw materials for industrial products, mostly in the form of panel products or moulded composites. The purpose of the present investigation is to quantify the effect of hygrothermal treatment on dimensional stability properties for wheat and hemp and to compare the results to wood fibres from beech and spruce.

This study is part of a research programme on characterisation and use of plantfibres for new environmentally friendly products.

## EXPERIMENTAL METHODS

### *Materials*

Norway spruce (*Picea abies*) and beech (*Fagus sylvatica*) fibres were used. All wood fibres were produced using the Asplund process. Defibration was carried out at a processing temperature of 170 °C, a presteaming pressure of 4 bar and a residence time of 4 min.

Fibres from wheat straw *Triticum spp.* was obtained from a modified Asplund type process. The majority of fibres were found as bundles rather than as single fibres.

Hemp fibres: Stems from hemp *Cannabis spp.* variety Fedrina were water retted for 96 hours at 35 °C. Following retting the fibres were separated from the stems by mechanical scutching.

All fibres were dried by forced air in a flash type drier.

All materials were stored in a freezer prior to use. This was to prevent any further drying and to avoid microbial decomposition during storage. In all cases the fibres were allowed to defrost prior to hygrothermal treatment.

### *Methods*

#### **Steam treatment**

The steam treatments (hygrothermal treatments) were carried out using an autoclave (Fig.1) capable of holding a stainless steel sample basket of maximum 0.75 m<sup>3</sup>. In order to treat the finely divided fibre material, a series of fibre baskets were manufactured where the body of the baskets was lined with 600 micron aluminium mesh. The treatments were done by setting the steam generator to the desired treatment temperature, with additional electrical heating of the main body of the autoclave. Because of the large volume of the autoclave, working pressure is reached only after approximately 2 minutes. Steam release and opening of lid is accomplished in approximately 1 minute. Treatment time is time at working pressure.

Fibres of Norway spruce, beech and wheat were treated at 160 °C, 170 °C, 180 °C or 190 °C. Wheat fibres were treated at 140 °C, 150 °C, 160 °C and 170 °C. Hemp fibres were only treated at 160 °C or 170 °C. The duration of treatment was 5, 10, 20, 30, 40, 50 or 60 minutes.



*Figure 1: Autoclave used for the hygrothermal treatment*

### **Sorption measurements**

To aid in the sorption analysis of fibre samples, a series of climate chambers were designed (Fig. 2). The relative humidity (RH) is controlled by mixing two air lines containing dry and saturated air. The required RH is set by the flow of each individual line.



*Figure 2: New climate chambers for improved sorption studies.*

The apparatus can operate at temperatures from 20 °C to 60 °C, and each chamber has its own balance for determining weights of samples, so eliminating the problem of exposing a sample to non-ideal conditions. Samples were placed in fine pored hydrophobic polyester bags, and left to equilibrate in the chamber for a given period of time. Each sample was then weighed on a balance using a rubber glove mounted in the door of the chamber. Once equilibrium was achieved at a given humidity, the settings were altered to move to the next humidity in the given series. A detailed account of the climate chambers is given in (Strømdahl 2000).

### **Analysis of chemical composition**

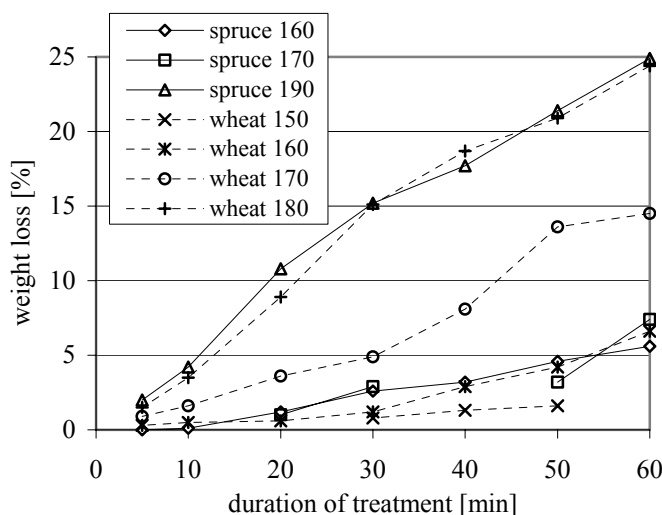
Determination of chemical composition was done by a gravimetric method with sequential removal of water soluble extractives, pectic substances, lignin and hemicellulose leaving the cellulose component in the sample. In all steps the samples were mechanically stirred. Between each step, the sample was recovered by filtration, dried at 70 °C for 16 hours and subsequently weighed. Initially, approximately 5 g of dried sample was ground to a fine powder. Determination of water solubles was done by adding 4 g of sample to 400 mL of demineralised water for 30 min at 25 °C. Pectic substances were determined by extraction with 300 mL 3 %

EDTA at pH 4 and 80 °C for 4 hours. Lignin was determined on approximately 2 g sample by oxidative removal using 10 g NaClO<sub>2</sub> and 20 ml 10% (v/v) acetic acid in 300 mL demineralized water. The sample was placed at 75 °C for 1 hour after which another 5 g of NaClO<sub>2</sub> was added (additional NaClO<sub>2</sub> was not added for wheat straw and hemp fibres). The oxidative treatment was continued until no dark spots could be seen. The oxidized sample was washed 3 times with 50 °C water, 2 times with 96 % ethanol and 1 time with acetone. Approximately 100 mL was used for each wash. Hemicellulose was extracted from the sample by 50 mL 25% NaOH and 4% 50 mL H<sub>3</sub>BO<sub>3</sub> for 90 min at 25 °C. Cellulose was determined as the remaining component excluding ash content. Ash was determined on the raw sample and the final cellulose fraction by incineration of the samples for 3 hours at 550 °C.

## RESULTS AND DISCUSSION

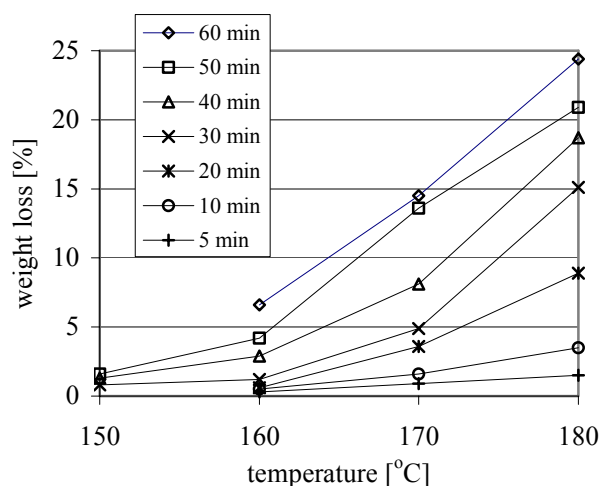
### *Weight loss from steam treatment*

Examples of weight loss as a function of temperature and duration of steam treatment are shown in, Figs. 3 and 4. In the case of Norway spruce fibres, the results obtained for experiments carried out at a temperature of 180 °C have been omitted due to obvious inconsistencies (weight increase).



**Figure 3:** *Weight loss as a function of duration of steam treatment for Norway spruce and wheat straw fibres treated at different temperatures*

The steam treatment results in weight losses as high as 25 %. Such massive weight loss is accompanied by dark discoloration. There is an almost linear relationship between weight loss and treatment time (Fig. 3). At the highest temperatures the weight loss appears to gradually decrease over time as would be expected. Temperature increase results in progressively increasing weight loss (Fig. 4). Wood fibres treated at 180 °C for half an hour or longer were visually ‘burnt’, and had a strong charred smell. Wheat straw fibres behaved similarly to wood fibres but at temperature levels some 10 °C below those of wood fibres emphasising the initial belief that wheat straw would be more susceptible to thermal degradation.



*Figure 4: Weight loss as a function of temperature and treatment for wheat straw fibres treated at different temperatures.*

### **Chemical composition**

For all species tested steam treatment causes a breakdown of the chemical structure. The extent of the breakdown increases with increasing treatment time and temperature (Tables 1-4). The most susceptible component to breakdown is hemicellulose. The typical pattern is a drop in hemicellulose content. However, spruce fibre hemicellulose showed an initial drop in hemicellulose content followed by an increase with treatment time and temperature. For cellulose the beech, hemp, and wheat fibres show only a slight decrease even at the highest temperatures and exposure times (Tables 2-4 and Fig. 5). Spruce cellulose is degraded by more than 50% at the highest temperatures and treatment times (Table 1 and Fig. 6). This observation is surprising and could indicate that spruce or maybe even softwoods in general are not suitable for this type of treatment. Pectic substances determined as EDTA extractable organic acids are only affected by the steam treatment to a minor degree. Even though wheat exhibited a high degree of weight loss, the annual plant fibres are less susceptible to chemical breakdown by steam treatment than wood (Tables 3 and 4).

For hemicellulose, lignin and extractives, the increase seen at the highest treatment times and temperatures is likely caused by degradation products such as anhydrous glucose, furfurals and tar-like compounds and not by the actual components. For spruce this is especially pronounced for the hemicellulose where a significant increase can be seen at temperatures above 170 °C (Table 1 and Fig. 6). The most likely source is alkaline extractable cellulose breakdown products. The figures should therefore be used for relative comparisons only, as the specificity of the chemical analysis does not allow for separation of degradation products and structural components. Only for cellulose which is the last residue remaining in the analysis, can the data be interpreted as being consistent with the actual cellulose content.

The thermal resistance of the annual fibres is somewhat surprising. It can likely be linked to the lower lignin content of these plants. This indicates that the initial starting point of the thermal degradation may be the formation of thermoradicals on the lignin and not the acidic hydrolysis of carbohydrates and low molecular weight compounds as described in (Elder 1991). This is also confirmed by the high degradability of the spruce cellulose. Spruce lignin is more condensed compared to beech, hemp and wheat and thereby has a higher oxidation potential. This may affect the ability of the lignin polymer to act as a radical scavenger or anti-oxidant protecting the cellulose from oxidative breakdown. The massive breakdown of spruce cellulose may therefore

be a combined effect where acid hydrolysis is enhanced by oxidative breakdown initiated by thermoradicals on lignin. Since the steam treatment is taking place under aerobic conditions the lignin radicals can facilitate the formation of activated oxygen species increasing the degree of oxidation even further.

**Table 1: Chemical composition of untreated and steam treated spruce fibres.**

Temp/time (°C/min)	Extractives (%)	Pectin (%)	Lignin (%)	Hemicell. (%)	Cellulose (%)
Untreated	7,0	1,5	24,6	20,8	46,1
160/10	7,3	4,0	32,0	17,7	39,0
160/50	16,2	3,0	30,7	19,6	30,6
170/10	10,6	3,4	32,9	14,8	38,4
170/50	15,5	3,2	31,6	23,7	26,0
180/5	13,2	4,1	30,8	19,3	32,6
180/30	15,1	3,8	32,0	28,1	21,0
180/40	12,5	4,2	32,7	28,5	22,1
180/50	12,4	2,9	35,2	18,4	31,1
180/60	9,5	3,0	38,2	29,9	19,3
190/10	15,4	2,5	30,3	17,3	34,5
190/50	7,6	3,7	41,4	30,1	17,2

**Table 2: Chemical composition of untreated and steam treated beech fibres.**

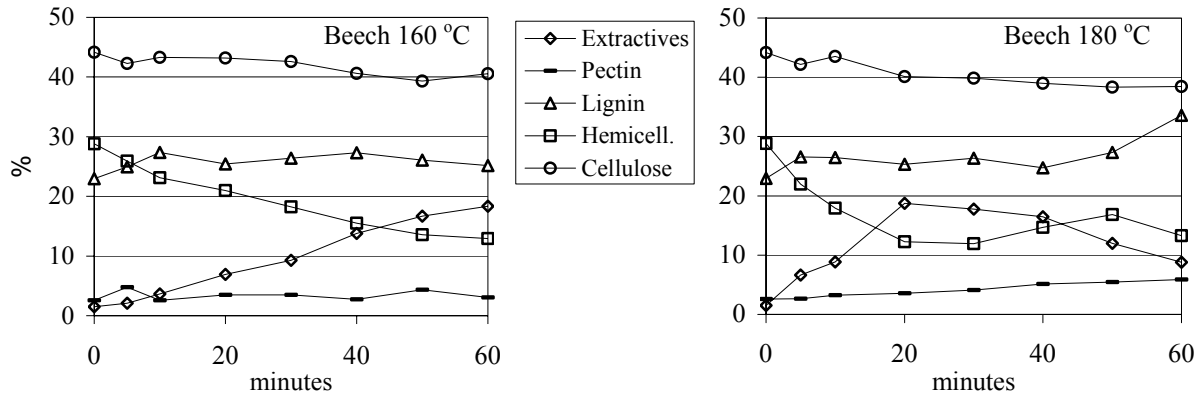
Temp/time (°C/min)	Extractives (%)	Pectin (%)	Lignin (%)	Hemicell. (%)	Cellulose (%)
Untreated	1,5	2,6	22,9	28,8	44,1
160/5	2,1	4,8	24,9	25,9	42,3
160/10	3,6	2,6	27,4	23,1	43,3
160/20	6,9	3,5	25,4	21,0	43,2
160/30	9,3	3,5	26,4	18,2	42,6
160/40	13,8	2,7	27,3	15,5	40,6
160/50	16,7	4,4	26,1	13,6	39,3
160/60	18,3	3,0	25,2	12,9	40,5
180/5	6,7	2,6	26,5	22,0	42,2
180/10	8,9	3,2	26,5	17,9	43,5
180/20	18,7	3,6	25,3	12,3	40,1
180/30	17,8	4,1	26,4	11,9	39,9
180/40	16,5	5,1	24,7	14,7	39,0
180/50	12,0	5,5	27,3	16,9	38,4
180/60	8,8	5,9	33,6	13,3	38,4

**Table 3: Chemical composition of untreated and steam treated hemp fibres.**

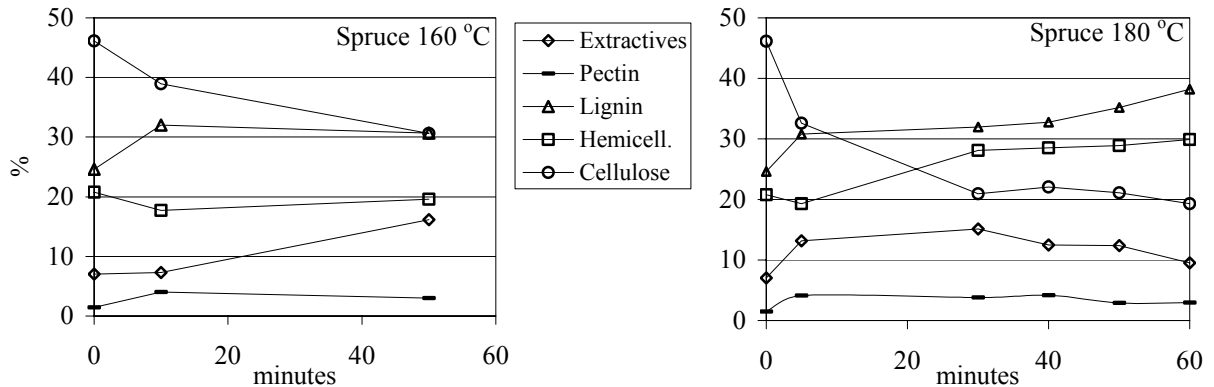
Temp/time (°C/min)	Extractives (%)	Pectin (%)	Lignin (%)	Hemicell. (%)	Cellulose (%)
Untreated	11,4	6,9	5,9	16,3	59,5
160/5	15,2	3,9	3,9	14,5	62,4
160/10	16,4	4,03	3,6	14,0	62,0
160/20	16,1	3,9	3,3	13,8	62,9
160/30	16,2	3,6	5,0	13,3	61,9
170/5	16,6	3,9	3,3	14,2	61,4
170/10	17,7	3,9	4,2	14,5	59,3
170/20	18,1	3,9	6,3	13,9	57,9
170/30	16,2	3,9	7,1	14,7	58,9

**Table 4: Chemical composition of untreated and steam treated wheat fibres.**

Temp/time (°C/min)	Extractives (%)	Pectin (%)	Lignin (%)	Hemicell. (%)	Cellulose (%)
Untreated	7,7	4,7	11,9	37,6	38,1
140/20	9,5	4,3	14,4	35,6	36,2
150/5	8,6	4,4	13,3	37,5	36,2
160/5	8,9	4,9	15,5	35,3	35,3
160/20	12,5	5,1	17,7	28,9	35,9
170/5	9,3	4,7	16,4	33,4	36,3



**Figure 5: Chemical composition of steam treated beech fibres as a function of time.**



**Figure 6: Chemical composition of steam treated spruce fibres as a function of time.**

**Sorption characteristics**

The majority of the data presented is from desorption experiments. If adsorption data is presented, this is specifically mentioned.

Fig. 7 shows isotherms for reference samples of the four species employed. Perhaps the most striking features are the similarities. The sorption behaviour of the two types of wood fibres is almost identical, and the annual plant fibres only deviates significantly in the very high range of relative humidity, where particularly hemp takes up an average of 40 % more moisture than wood fibres. Such behaviour may be due to a larger proportion of micropores available to capillary condensation or it may be caused by a higher concentration of moisture-cluster forming ions (Salmén 1997). For the very low range of relative humidity, wheat appears to be slightly less hygroscopic than the three other species.



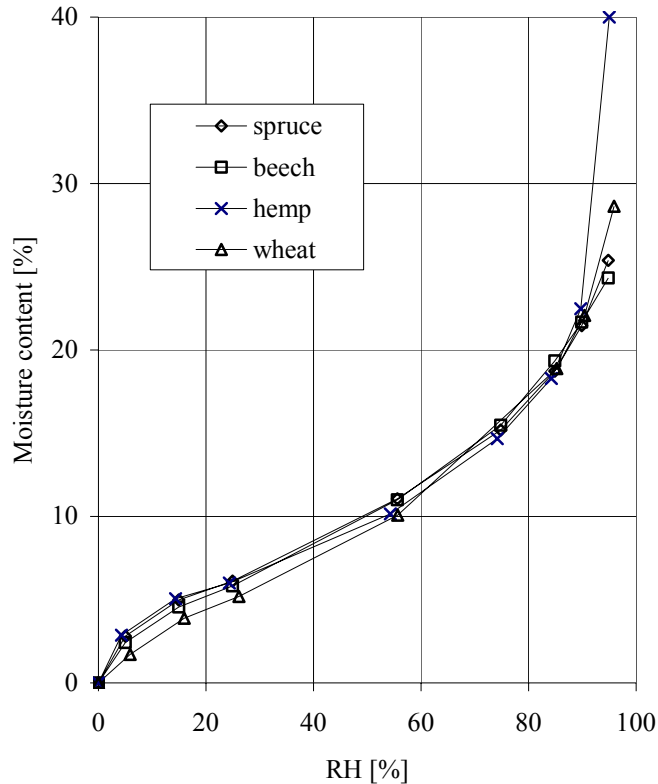


Figure 7: Isotherms (20 °C) for non-treated reference samples of Norway spruce, beech, hemp and wheat

Because of the large amount of data from the steam treatment experiments a concentrated presentation is made. For this purpose a ratio,  $R_{rh}$ , is introduced which expresses the equilibrium moisture content of a treated sample relative to a non-treated sample (reference) at a particular relative humidity. Two ratios  $R_{55}$  and  $R_{95}$  are chosen ( $RH \cong 55\%$  and  $RH \cong 95\%$ ) to cover both the pure surface sorption range and the range of potential capillary condensation (Table 5).

The numerous combinations of treatment temperatures and durations of treatment reveal a general pattern of the effect of steam treatment on the subsequent capability of moisture uptake. Fig. 8 illustrates this pattern. A mild treatment results in a reduction of sorption at all levels of RH although relatively more pronounced the lower the level of RH. At progressively longer duration of treatment or progressively higher temperatures the behaviour is different for low/medium RH and high RH.

For low and medium range RH ( $< ca. 85\%$ ) the reduction of sorption continues until a lower limit is reached (e.g. Fig. 8:  $R_{55} \cong 0.63$ ). The reduction of sorption continues to develop at a faster rate the lower the RH. This behaviour corresponds to the reduction of the number of primary sorption sites primarily on the hemicellulose fraction, as this fraction is the most sensitive to the steam treatment (Tables 1-4).

For high range RH ( $> ca. 85\%$ ) two additional mechanisms may be active. One is the capillary sorption in micropores created as a result of the thermal degradation of cell wall material. A second mechanism may be the gradual filling of such micropores by lignin made to flow by further steam treatment. As a result of these counteractive mechanisms, sorption at high RH in steam treated fibres may first grow (even beyond the level of untreated fibres), later drop (compare Figs. 8-9) and ultimately settle at a level corresponding to pure sorption at primary sorption sites.

**Table 5: R-ratio as a function of temperature and duration of treatment for fibres of Norway spruce (N), beech (B), hemp (H) and wheat (W)**

id.	RH [%]	temp. [°C]	duration of treatment [min]						
			5.0	10.0	20.0	30.0	40.0	50.0	60.0
N	95.0	160	0.90	0.78		1.02		0.90	1.06
N	95.0	170	0.89	0.96		0.87		0.88	0.80
N	95.0	180	0.97		1.02	1.20	0.99	0.95	0.85
N	95.0	190	0.84	0.97	0.88	0.81	0.75	0.69	0.69
N	55.0	160	0.93	0.80		0.77		0.69	0.74
N	55.0	170	0.88	0.85		0.77		0.70	0.67
N	55.0	180	0.78		0.68	0.69	0.69	0.67	0.64
N	55.0	190	0.80	0.68	0.67	0.66	0.68	0.69	0.69
B	95.0	160	0.98		0.93	0.91	0.93	1.01	1.02
B	95.0	170				1.11	1.00	0.82	
B	95.0	180	0.91		1.16	1.11	1.03	0.84	0.78
B	95.0	190			0.91	0.84	0.72		
B	55.0	160	1.01	0.93	0.89	0.83	0.82		0.76
B	55.0	170				0.71	0.76	0.73	
B	55.0	180	0.90		0.68	0.63	0.65	0.66	0.63
B	55.0	190			0.62	0.62	0.64		
H8	95.0	160	1.16	1.20	1.21	1.13			
H32	95.0	170	1.23	1.22	1.35	0.95			
H8	55.0	160	0.93	0.87	0.83	0.79			
H32	55.0	170	0.98	0.93	0.89	0.81			
W	95.0	150	1.01	1.31	1.34	1.04			1.10
W	95.0	160	0.98		0.99	1.04			1.23
W	95.0	170	0.99	1.29	1.43	1.19			1.27
W	95.0	180	1.14	1.19	1.53	1.21			1.56
W	95.0	190		1.29	1.13	1.04			1.05
W	55.0	150	1.01	1.11	1.11	0.97			0.86
W	55.0	160	0.99		0.94	0.85			0.74
W	55.0	170	0.94	1.00	0.89	0.71			0.69
W	55.0	180	1.00	0.89	0.83	0.69			0.84
W	55.0	190		0.79	0.77	0.67			0.75

Because the chemical composition is different for the four fibre species, different sorption behaviour is to be expected, depending *e.g.* on the thermal degradability of holocellulose and inclination to flow of the lignin specific to the species. The sorption behaviour of Norway spruce follows closely the patterns shown in Figs. 8 and 9 for beech. For both species the lower limit for sorption corresponds to an  $R_{55}$ -ratio of the order 0.60 – 0.65. For high values of RH the isotherms occasionally cross the reference isotherm. However, the  $R_{95}$ -ratio rarely goes higher than  $R_{95} = 1.15$ . Severe treatments produce  $R_{95}$ -ratios of the order 0.70 – 0.75. The apparent increase in hemicellulose content for spruce at high temperatures (Table 1) is not accompanied by an increase in equilibrium moisture content, indicating that the cellulose degradation products do not offer any sorption sites.

The sorption behaviour of the annual plant fibres follows the general patterns of the wood fibres. However, the effect of steam treatment is slightly less with the lower limit of sorption corresponding to  $R_{55} = 0.70 - 0.75$ . For high values of RH the isotherms generally cross the reference isotherm (*e.g.* Fig. 10) and  $R_{95}$ -ratios goes as high as 1.5. Severe treatment may produce  $R_{95}$ -ratios of the order 1.0 – 1.1. Contrary to the results of the chemical analysis, it appears that the annual plant fibres are more easily degraded than the wood fibres, for which reason more capillary sorption is seen. This may be confirmed from Fig. 3, which suggest the

weight loss for wheat at 180 °C to be comparable to that for Norway spruce at 190 °C. In correlation with the lower lignin content, the lignin flow in annual plants seems to be not as efficient with respect to the filling of micropores. In the low/medium range of RH the lower thermal degradation of the annual plants is in accordance with the sorption properties.

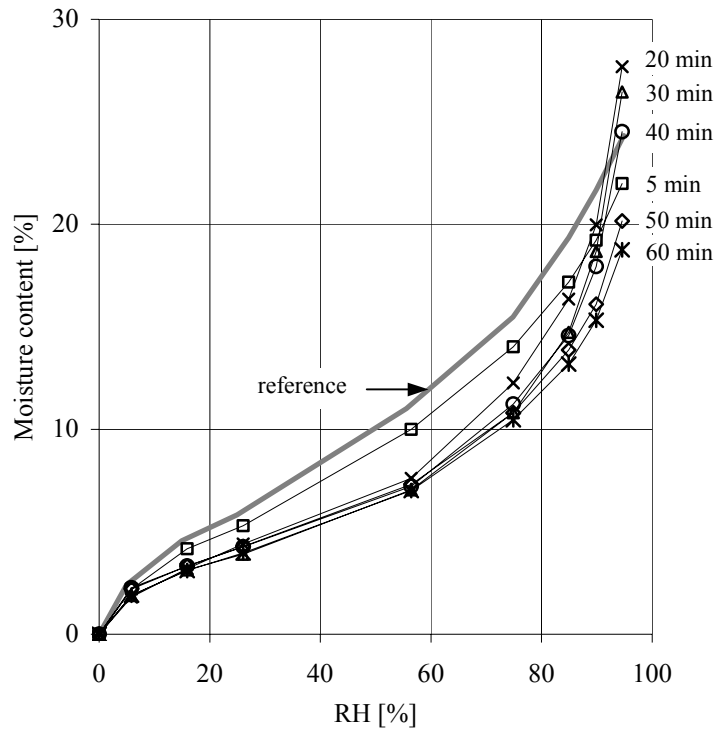


Figure 8: Isotherms for steam treated beech. Treatment temp.: 180 °C. Duration of treatment: 5 – 60 min.

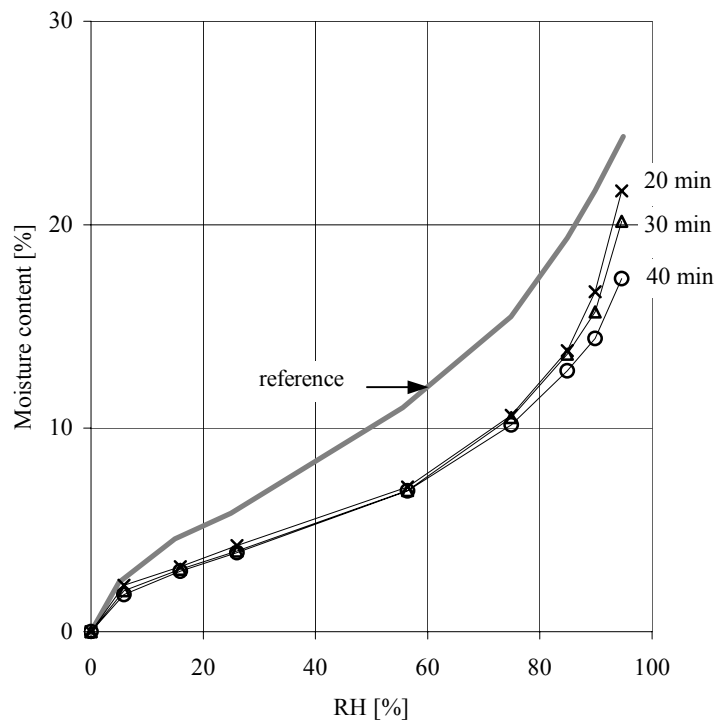


Figure 9: Isotherms for steam treated beech. Treatment temp.: 190 °C. Duration of treatment: 20 – 40 min.

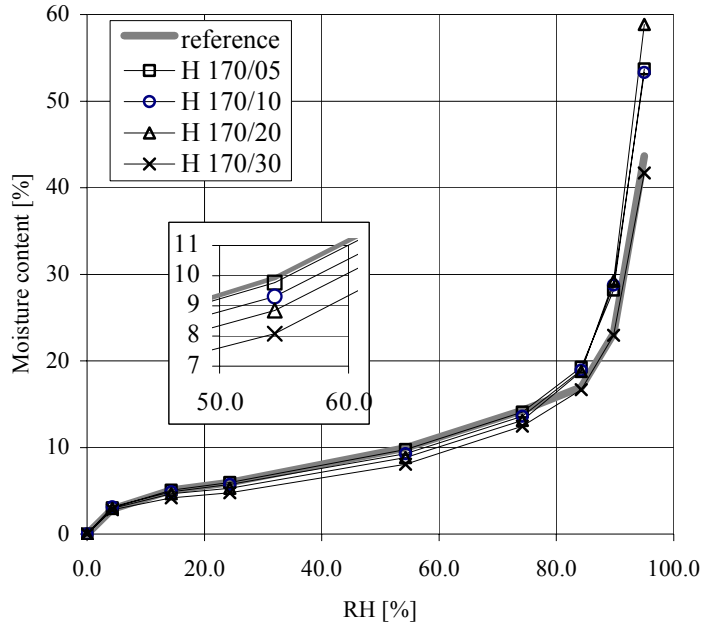


Figure 10: Isotherms for steam treated hemp. Treatment temp.: 170 °C. Duration of treatment: 5 – 30 min.

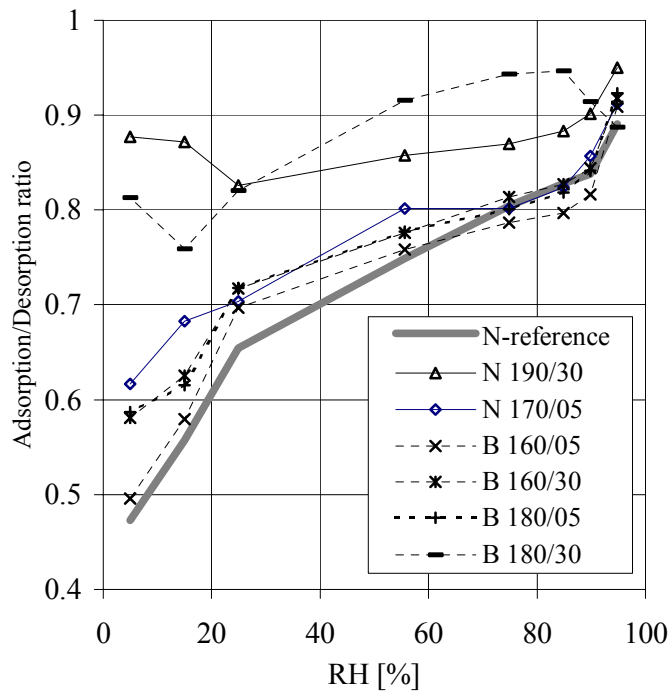


Figure 11: Adsorption/desorption ratio for steam treated beech and wood fibres

Adsorption experiments were carried out for a limited number of samples. The ratio between adsorption moisture content and desorption moisture content (A/D-ratio) follows the general patterns for wood. The A/D-ratio is low for low RH and grows to about 0.9 for high values of RH. Steam treatment produce a significant increase in the A/D-ratio, and heavy treatment leaves the A/D-ratio at 0.85-0.90 throughout the entire range of RH (Fig. 11). Steam treatment appears to makes it easier for water molecules to re-open cell wall structural bonds formed during drying. Hemp fibres behaves differently and do not show any significant hysteresis in the range RH = 0.2–0.8. However, for high RH hemp shows a very large hysteresis with A/D-ratios as low as 0.6

(Fig. 12). Such behaviour indicates that untreated hemp fibres – contrary to wood fibres – hold a significant proportion of micropores and that the number of micropores is increased by steam treatment. The adsorption results for wheat were not consistent and it can only be concluded that wheat fibres – like hemp fibres – show very little hysteresis over the medium range of RH.

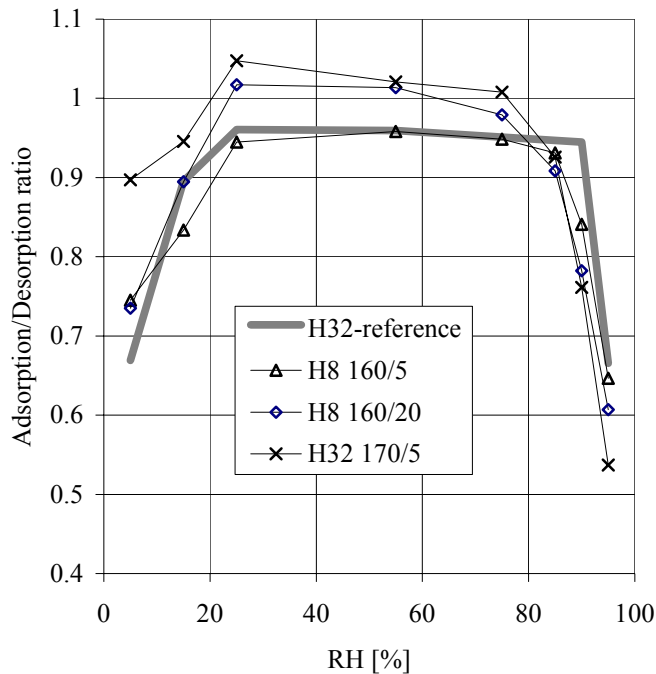


Figure 12: Adsorption/desorption ratio for steam treated hemp

A major reason for heat treating fibres is that the reduced sorption is reflected in improved dimensional stability. A proper measure of the efficiency of steam treatment with respect to dimensional stability is the  $R_{55}$ -ratio. The  $R_{95}$ -ratio is not to be used for that purpose; it merely serves as an indicator of capillary sorption, which does not give rise to significant dimensional movements.

## CONCLUSION

Steam treatment of fibres from selected species of wood and annual plants can lower the equilibrium moisture content of the fibres. A mild treatment results in decreased sorption at all levels of RH. For more severe treatments there is a continued reduction of sorption *af* RH values below approximately 85 %. For higher values of RH the initial reduction of sorption is followed by an increase caused by capillary condensation in micropores produced as a result of the hygrothermal treatment. For the wood fibres lignin flow will eventually fill the micropores and a reduction of sorption is then seen throughout the entire range of RH values.

Hygrothermal treatment also causes a thermal breakdown of the fibres with the hemicellulose component as the most affected. A surprising observation was the fact that cellulose in spruce was extensively degraded compared to the other species tested.

## ACKNOWLEDGEMENTS

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**ANALYSIS AND TESTING PROPERTIES**  
POSTER PRESENTATIONS





## Glulam of Heat-treated Wood – Delamination Test

Charlotte Bengtsson<sup>1</sup>, Jöran Jermer<sup>2</sup> and Anders Clang<sup>3</sup>

SP Swedish National Testing and Research Institute, Wood Materials and Structures, Box 857, SE-501, 15 Borås, Sweden: <sup>1</sup>charlotte.bengtsson@sp.se, <sup>2</sup>joran.jermer@sp.se, <sup>3</sup>anders.clang@sp.se

**Keywords:** heat-treated wood, glulam, delamination

### ABSTRACT

A study was carried out to compare the performance of glulam of heat-treated wood with glulam of untreated wood with respect to the gluability properties. The heat-treated wood was treated to comply with performance requirements for above-ground end-uses. Small glulam beams were made of untreated and heat-treated pine and spruce. Two different adhesives, PRF (Phenol-Resorcinol-Formaldehyde) and PVAc (Poly-Vinyl-Acetate) were used. A delamination test was carried out according to EN 391, method B. The study confirmed that gluing of heat-treated wood needs special consideration. The PRF adhesive performed very well whereas the PVAc adhesive showed an unacceptable percentage of delamination and thus seems to be unsuitable for gluing heat-treated wood, at least without modification of the gluing process.

### OBJECTIVE

To compare the performance of glulam of heat-treated wood with glulam of untreated wood with respect to the gluability properties.

### MATERIAL

Small glulam beams, length 700 mm and depth 130 mm, with 16 mm laminations were made of heat-treated and untreated pine (*Pinus sylvestris*) and spruce (*Picea abies*). Two different adhesives, one PRF (Phenol-Resorcinol-Formaldehyde) and one PVAc (Poly-Vinyl Acetate) adhesive were used. Details of the gluing are given in Table 1.

*Table 1. Details for the gluing of beams.*

	<b>PRF</b>	<b>PVAc</b>
Adhesive/hardener	Cascosinol 1711/2620	Cascol 3333/3334
Mix adhesive/hardener	100/20	100/6
Amount of adhesive [g/m <sup>2</sup> ]	400	200
Closed waiting time [min]	30	12
Pressure [MPa]	0.7	0.7
Pressure time [h]	4	1

The heat-treatment was carried out at maximum temperature of 220°C during five hours and the total process time was four days. The process was completed by conditioning so that the MC after the treatment was approximately 6%. This level of treatment was classified as suitable for timber to be used for outdoor exposure above ground, i.e. hazard class 3 according to EN 335-1.

## METHOD

75 mm specimens were cut from each glulam beam and delamination was carried out according to EN 391, method B.

## RESULTS

The results, expressed as percentage delamination, are presented in Tables 2 and 3.

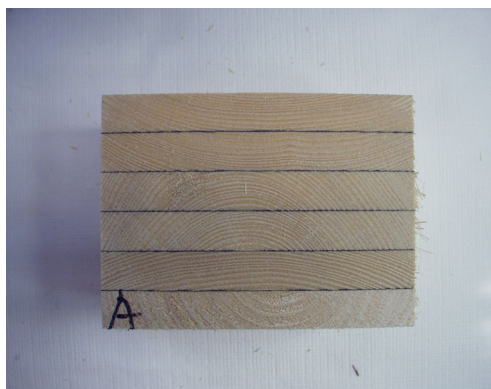
*Table 2. Delamination [%] for glulam specimens bonded by PRF adhesive before and after delamination test.*

PRF Sample no	Heat-treated spruce		Untreated spruce		Heat-treated pine		Untreated pine	
	Before	After	Before	After	Before	After	Before	After
1	--	--	--	--	--	--	--	--
2	--	--	--	--	--	2.6	--	--
3	--	--	--	--	--	--	--	--
4	--	--	--	--	--	1.9	--	--
5	--	--	--	--	1.5	6.9	--	--
6	--	--	--	--	--	2.3	--	--
Average						2.3		
St. dev.						2.5		

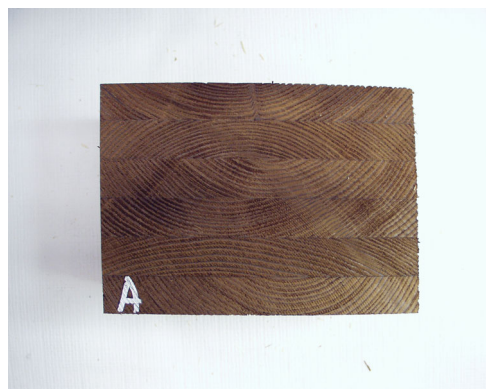
*Table 3. Delamination [%] for glulam specimens bonded by PVAc adhesive before and after delamination test.*

PVAc Sample no	Heat-treated spruce		Untreated spruce		Heat-treated pine		Untreated pine	
	Before	After	Before	After	Before	After	Before	After
1	32.3	72.7	--	24.2	18.8	73.1	--	36.2
2	36.5	64.6	--	20.8	20.8	52.7	--	34.6
3	50.8	55.8	--	14.2	24.6	70.0	--	40.8
4	50.4	74.6	--	14.2	24.5	68.1	--	53.5
5	44.6	65.8	--	16.5	21.9	64.2	--	40.4
6	49.6	69.2	--	10.0	27.3	59.2	--	63.8
Average	44.0	67.1		16.7	22.5	64.6		44.9
St. dev.	7.9	6.8		5.1	3.0	7.5		11.4

The figures below shows four specimens before the delamination test. For some specimens bonded by PVAc the outer lamination fell off even before the test.



a)



b)



c)



d)

- a) Untreated spruce bonded by PRF
- c) Untreated pine bonded by PVAc

- b) Heat-treated spruce bonded by PRF
- d) Heat-treated spruce bonded by PVAc

### CONCLUSIONS

The study confirms that gluing of heat-treated timber needs special consideration.

The PRF adhesive performed very well in this study whereas the PVAc adhesive showed an unacceptable percentage of delamination. The hydrophobic wood surface is probably the most important reason for the latter as it causes a slower penetration of the solvents from the glue to the surrounding wood. PVAc thus seems to be unsuitable for gluing heat-treated wood, at least without modification of the gluing process.

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- EN 391 Glued laminated timber – Delamination test of glue lines.



## Soft Rot Decay in Acetylated Wood: Microcalorimetry and Ergosterol Assay in Decayed Wood

Behbood Mohebb<sup>1,2</sup>, Carsten Mai<sup>1</sup> & Holger Militz<sup>1</sup>

<sup>1</sup> Institute of Wood Biology and Technology, Büsgenweg 4, 37077 Göttingen, Germany

<sup>2</sup> Tarbiat Modarress University, P.O. Box 14155-4838, Tehran, Iran

E-mail: bmohebb@gwdg.de & mohebb@modares.ac.ir ; E-mail: cmai@gwdg.de ; E-mail: hmilitz@gwdg.de

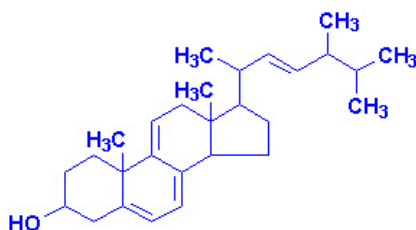
**Keywords:** Soft rot decay, Beech (*Fagus sylvatica*), acetylation, ergosterol assay, microcalorimetry.

### ABSTRACT

Acetylation significantly inhibits microbial decay of wood in ground contact (mainly soft-rot). Microcalorimetry and ergosterol determination were applied to quantify microbial activity within soil exposed wood. While microcalorimetry determines the heat production, *i.e.* the total activity of all microorganisms, ergosterol determination is a special indicator for fungal activity. Both methods revealed that an increased degree of acetylation led to a reduction of microbial activity and fungal biomass in the wood. These results show that the extent of colonisation of wood is reduced with increasing degree of acetylation.

### INTRODUCTION

Fungal bioactivity may be assessed by various methods: mass loss of substrate, increased mass of fungus, linear hyphal growth, ergosterol content, chitin content, CO<sub>2</sub> production, heat production, O<sub>2</sub> consumption, or ATP concentration. As *heat* is released in all metabolic processes in plants, animals and microorganisms, *isothermal calorimetry* or *microcalorimetry* is a powerful method to study these processes. The heat released is proportional to growth and consumption of nutrients, as long as the metabolic processes are constant. Isothermal calorimetry is the measurement of heat and heat production rates under essentially isothermal conditions (Bjurman and Wadsö 2000, Xie *et al.* 1997) and is a rapid method to determine bioactivity of microorganisms in decaying wood.



**Fig. 1:** Ergosterol (24,β-methylchlesta-5,7,trans-22-trien-3,β-ol)

Ergosterol (24,β-methylchlesta-5,7, trans-22-trien-3,β-ol) (Fig. 1) is a steroid and a prominent membrane component of most fungi, which has frequently been used as fungal-index molecule in natural substrates and it is not found in native wood (Encinas and Daniel 1999, Weete 1980, Karen 1997). The ergosterol assay is used to estimate the fungal biomass in wood. Ergosterol analysis can also be used for detecting and quantifying fungal biomass of various biological

materials, such as soils (West *et al.* 1987), seeds (Seitz *et al.* 1977) and mycorrhizae (Salmanovicz and Nylund 1988).

The influence of acetylation on wood bioresistance is now well known. However, it has been reported that fungal hyphae were detected in the lumina of acetylated wood but could not attack acetylated cell walls (Mohebby and Militz 2002, Peterson and Thomas 1978). However, the degree of colonisation with regard to the degree of acetylation was not yet determined in detail. A combination of techniques to measure microbial activity with determination of weight loss of wood could help to distinguish between wood degradation and colonisation without decay.

In this paper, we report on microcalorimetry and ergosterol assay, two sensitive methods to monitor total microbial activity as well as fungal biomass in acetylated wood.

## MATERIAL AND METHODS

### *Sample preparation*

Mini-stakes of Beech (*Fagus sylvatica*) with sizes 5×5×110 mm were acetylated with acetic anhydride and acetic acid at temperature between 80-120°C and vacuum of about 0.97 bar for 180 minutes (Beckers and Militz 1994, Beckers *et al.* 1994). The obtained percentages of weight gains were 1.84, 6.72, 8.33 and 17.43%. Soil boxes (43 × 32 × 21 cm) were prepared according to European Standard ENV 807 and filled with John Innes II soil. Sample were planted into the soil at 95% of its water holding capacity and kept under controlled conditions (temperature 26±1 °C and relative humidity 65±5%).

### *Microcalorimetry*

Heat production was monitored in a microcalorimeter with twin measuring background correction (2277 Thermal Activity Monitor, TAM: ThermoMetric, Jarvalla, Sweden). Glass ampoules (2.5ml) with Teflon seals and stainless steel lids were used as sample vials. Wood specimens with sizes about 5 × 5 × 20 mm were cut from the eroded end of soil-exposed mini-stakes. They were kept in a refrigerator under 4°C. Cut specimens were kept at room temperature (25°C) for 1 h to reach room temperature and reactivate the microorganisms. After conditioning, they were placed in the glass ampoules and held for few minutes at the equilibrium position and then lowered down into the channel gently. Internal calibration was carried out at 300µW in a static mode. The detection limit was ±1 µW and the control was an empty vial. Average heat production and produced energy rates were recorded at intervals of 10 seconds for 24 hours. The program DIGITAM 2.0 (SciTech Software, ThermoMetric, Jarvalla, Sweden) was used to record the heat production. Correction was carried out based on dry weight of the specimens (Bjurman and Wadsö 2000, Xie *et al.* 1997).

### *Ergosterol assay*

Wood samples were crushed with a knife and transferred into homogenisation vessels, and then homogenised in liquid nitrogen by Ultra-Thurrax. Homogenised wood was conditioned at room temperature to reach equilibrium moisture content for about 24 hours. Their moisture contents were determined in an oven at 105±3°C to measure dry weight of the samples. About 1.5g of samples were added into bottles containing KOH 10% in methanol (25ml) and 2,6-Di-tert-butyl-4-*P*-cresol (= 2,6-Di-tert-butyl-4-methylphenol= (C<sub>6</sub>H<sub>24</sub>O); BHT) (200ppm). They were heated at 60°C for 30 minutes in a water bath and then cooled down. About 4ml of extracted samples were transferred into Pyrex tubes (10ml) and 2ml n-Hexane was added to the tubes. They were mixed very well. Then 4ml of de-mineralised water was added into the tubes and shaken for 10 minutes. Samples were centrifuged at 2000 r/min for 5 minutes. n-Hexane phase (1ml) in the tubes was pipetted into HPLC vials and dried in a vacuum chamber at 50°C. The residue in the

vials was dissolved in 300µl methanol (Braun-Lüllemann, 1995; Hendel & Marxsen, 2000) and ergosterol content was determined by HPLC (Hewlett-Packard Series 1100). Mobile phase was methanol 93% that was run with a flow-rate of 1.5 ml/min and an injection volume of 20 µl was generally used in three replicates. Ergosterol standards (10, 50, 100 and 200 µl) were used to calibrate the HPLC after measuring of every 30 samples. Retention time for ergosterol was between 10-11 minutes.

## RESULTS AND DISCUSSION

### *Ergosterol assay*

The amount of ergosterol in the acetylated and the non-acetylated beech wood was determined during 300 days of exposure to soil beds (Fig. 2). The ergosterol content increased during the first and second month of exposure to the soil and then it decreased. Comparison between acetylated and non-acetylated wood reveals that the decreased amount of ergosterol could relate to the degree of acetylation. In non-acetylated wood, the ergosterol content is higher than the acetylated wood and it was not detectable at the highest weight gain. After 300 days, the ergosterol in the non-acetylated wood decreased to a similar amount in moderately acetylated wood.

The initial increase in ergosterol content indicates rapid colonisation of fungi in the wood, when fungi assimilate organic compounds from the soil. After consumption of the major amount of nutrients from the soil, the amount of ergosterol decreased due to lack of nutrients. In this phase fungi metabolized their reserved ergosterol in mycelial walls (Braun-Lüllemann 1989). Anatomical structure of the beech wood such as open vessel lumina and readily available nutrients in ray cells may have contributed to the early and rapid colonisation of the fungi through the vessels, ray cells and axial parenchyma in beech wood. Fungal succession could be considered as another reason for the varying ergosterol quantity during exposure to the soil. Käärrik (1975) reported successional changes in the colonising microorganisms and also successive changes in the attacking decay fungi.

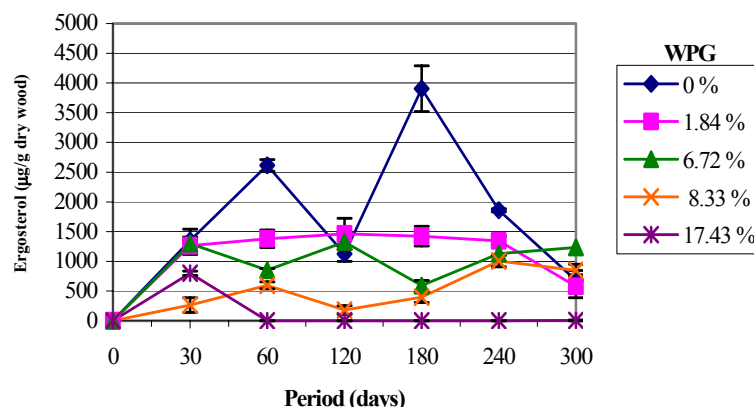


Fig. 2: Ergosterol content in acetylated beech wood

Our results confirm other reports that an early and rapid colonisation and then reduction of a blue stain fungus, *Lasiodiplodia theobromae*, occurred in birch and pine based on the measurements of ergosterol (Encinas and Daniel 1999) and the same was also reported for *Ceriporiopsis subvermispora* (Messner *et al.* 1998).

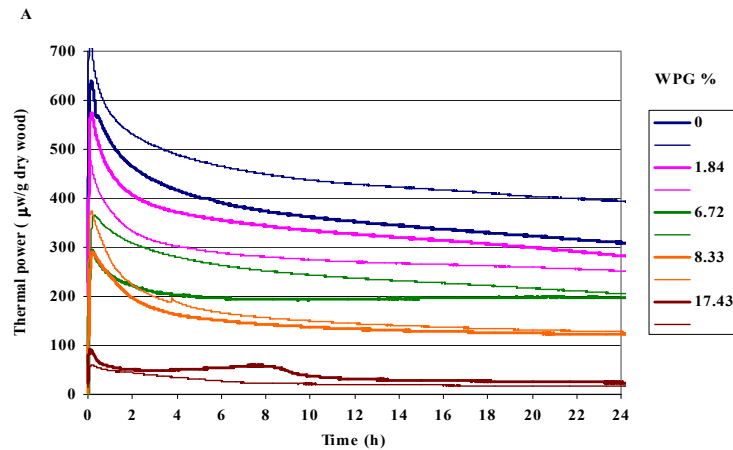


Regarding the above explanation, the colonisation phase occurs in the non-acetylated and the acetylated wood. However, fungal biomass reduces with raising the weight gains and was not detectable at the highest weight gain. Due to their inability to degrade the acetylated cell wall, fungi do not find nutrients in wood and probably metabolised deposited ergosterol in mycelial walls.

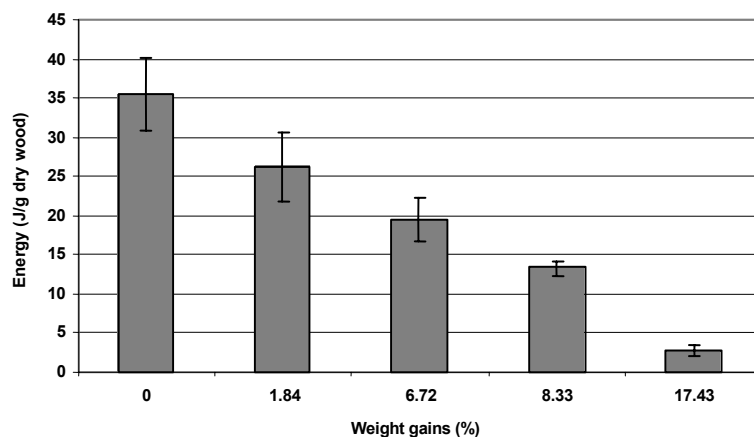
The presence of fungal mycelia was revealed in highly acetylated wood by microscopy in our previous work (Mohebbi and Militz 2002). It could either be that the amount of ergosterol in these hyphae was under the detection limit or that the hyphae did not contain ergosterol, due to metabolic degradation and oxidation upon cell death (Gessner and Schmitt 1996).

### ***Microcalorimetry***

Microcalorimetric studies during 24 hours revealed that microbial metabolism was decreased with raising weight gains (Fig. 3). Heat production tended to decrease over time, most probably due to oxygen depletion in the vials. Total energy production after 24 hours showed that microorganisms produced the lowest amount of energy at the highest weight gain. The highest amount of energy was produced in the non-acetylated wood (Fig. 4).



***Fig. 3: Heat production in non-acetylated and acetylated beech wood***



***Fig. 4: Total energy production in non-acetylated and acetylated beech wood after 24 hours***

Microcalorimetry revealed that the bioactivity of soil microorganisms decreased with increasing degree of acetylation. The same tendency was confirmed by ergosterol measurements. Ergosterol measurements additionally revealed that fungi also contributed to the colonisation of wood

mainly during the early period of exposure. However, their mass decreased due to lack of nutrients especially when cell wall degradation was prevented by acetylation.

Ergosterol assay and microcalorimetry are powerful methods to monitor microbial activity and biomass in acetylated wood. Increased degree of the acetylation correlates with reduced ergosterol content in wood and lower heat production. Ergosterol revealed that the amount of the fungal colonisation correlates with the degree of acetylation.

### ACKNOWLEDGEMENTS

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## Exterior Durability of Coatings on Modified Wood

J.G. Nienhuis<sup>1</sup>, B. van de Velde<sup>1</sup>, W.N.H. Cobben<sup>1</sup>, E.P.J. Beckers<sup>1</sup>

<sup>1</sup> SHR Timber Research, The Netherlands, Nieuwe Kanaal 9b 6709 PA WAGENINGEN,  
j.nienhuis@shr.nl

**Keywords:** exterior durability, coatings, modified wood, thermal, acetylation

### ABSTRACT

Artificial weathering of coated modified wood showed better performance of the coating. Results of 4 ½ and 5 year outdoor weathering of acetylated and thermally treated wood showed excellent performance of the coating compared to untreated wood. For exterior durability, the main improvement of the coating performance was demonstrated by water borne coatings, which showed less blistering, flaking and cracking on acetylated wood. Exterior performance of the coating on thermally treated wood is better or is at least comparable to a coating on untreated wood.

### INTRODUCTION

Modification of wood by thermal or chemical modification results in altered cell walls. It is believed that the wood structure is no longer recognised or less recognised by wood destroying fungi, which results in longer durability. Chemical modification often results in a reduction of swelling (Rowell 1983, Kumar 1984). For acetylation, acetic anhydride reacts with wood hydroxyl groups. This reaction leads to a permanent swollen state of the wood and the hydrogen bond forming capacity of unreacted hydroxyl groups is strongly reduced. Dimensional changes can be reduced by up to 80 % by acetylation compared to untreated wood (Beckers and Militz 1994, Goldstein *et al.* 1961, Rowell and Plackett 1988).

Re-polymerisation of wood by thermal treatment also results in a changed structure of the wood: hydroxyl groups are less accessible by water, which results in an initial shrinkage of the treated wood species and a reduction of 40 % in hygroscopicity afterwards. Reduced water uptake leads to an increased dimensional stability (Tjeerdsma *et al.* 1998). Less swelling and shrinkage of the wood results in less stress on a coating. This enhances durability of the coating system on exterior used wood (De Meijer 2002). Water borne acrylics are, depending on their formulation, more elastic than solvent borne alkyds. Solvent borne alkyds are more commonly used for exterior topcoats due to their gloss, aesthetics and ease of application. However, due to ongoing oxidative drying, they show increased cross-linking, resulting in a brittle coating. On a permanently shrinking and swelling substrate, this result in cracks, flaking of the paint and an unprotected substrate. Therefore, a more dimensionally stable substrate, as obtained by modification, is believed to result into better outdoor durability of applied coatings.

### EXPERIMENTAL METHODS

L-joints made of thermally modified *pinus radiata* (unknown process) were coated with an opaque commercial solvent borne alkyd system and commercial water borne acrylic system, applied in a layer thickness of 80 – 100 µm in two layers. The endgrains of the L-joints were sealed with a water impermeable coating. The L-joints were exposed facing South at the exposure site of SHR Timber Research in Wageningen, the Netherlands since 1998.

Panels of acetylated Scots pine sapwood were exposed since 1995 at the exposure site of SHR Timber Research. Panels were placed on a rack facing South in an angle of 45°. The panels were coated with commercial waterborne and solvent borne coatings, both opaque and transparent ones applied in a layer thickness of 80 – 100 µm in two layers. As a reference, non-modified Scots pine sapwood panels were coated and exposed. Before exposition, some panels were damaged by artificially applied hail.

The paint systems were evaluated on cracking and flaking and surface moulds. The wood was evaluated on cracking and, for the L-joints, on open joints.

Cracking was evaluated according to ISO 4628 Part 4: Designation of degree of cracking. The evaluation is described by a number for the quantity (0 = no cracks, 5 = high density of cracks) and a number for the Size (0 = not visible, 5 = larger than 5 mm). 2S3 indicates: Quantity = 2 and Size = 3.

Flaking was evaluated according to ISO 4628 Part 5: Designation of degree of flaking. The evaluation is described by a number for the quantity (Flaked area %: 0 = 0%, 5 = 15% flaking) and a number for the Size (0 = not visible, 5 = larger as 30 mm). 2S3 indicates: Quantity = 2 and Size = 3

Performance of the exterior durability of paint systems was evaluated for thermally modified wood after 4 ½ years and for acetylated wood after 5 years.

## RESULTS AND DISCUSSION

### *Thermally treated wood*

#### **Opaque solvent borne alkyd (white colour)**

The untreated *pinus radiata* L-joints did not show any wood deterioration. The paint system showed some cracking on the edges or around the joint (1S5). It is known that this paint system, used as a primer, is susceptible for cracking on edges. The paint on the thermally modified L-joints showed the same pattern for cracking: some cracking was observed on the edges or around the joint (1S5). Cracking did not result into flaking.

#### **Opaque water borne acrylic (white colour)**

On one of the untreated L-joints, some light cracking was observed (1S3). The other L-joint did not show any cracking. The same results could be observed for the treated L-joint. One joint was open for 8%. This one showed cracking.

### *Acetylated wood*

#### **Transparent solvent borne alkyd (teak colour)**

Untreated samples of Scots pine sapwood showed severe flaking from 5S3 to 5S5. After severe cracking (from 2S3 to 3S), flaking was observed. All samples showed cracking due to hail damage and deep cracks in the wood. One sample showed severe wood decay. Treated samples did not show flaking. Some cracks were observed on edges and due to natural hail damage. Artificially damaged panels by hail simulation showed the same performance of the paint system compared to undamaged systems.

#### **Transparent water borne acrylic (teak colour)**

Only one untreated sample showed some flaking. The other panels were intact. Limited cracking was observed (from 1S3 tot 2S4) on cracks in wood and damaged paint film. On the acetylated

samples less cracking was observed (all 1S3). Severe dirt retention was observed. Panels damaged by artificial hail simulation did not result into cracks.

**Opaque solvent borne alkyd (white colour)**

Untreated samples showed severe flaking (3S3 to 5S4). After severe cracking (from 2S3 to 3S3) flaking was observed. Three samples showed deep cracks in the wood. The paint surface was coloured green by algae. The acetylated panels did not show flaking. Some cracking, also in the wood, was observed. Algae attack on the surface was strong. Panels damaged by artificial hail simulation did not show any cracking.

**Opaque water borne acrylic (white colour)**

Some flaking was observed on two untreated panels. Cracking initiated flaking. The untreated samples showed relatively more cracking (1S3 to 3S3) compared to the treated ones. Some samples showed blisters and one sample showed wood decay. The treated samples showed none to light cracking (1S3). Main cause of cracking was hail damage. Panels damaged by artificial hail simulation showed light cracking. One untreated sample showed flaking.

**Discoloration on acetylated wood**

In accelerated weathering tests, acetylated wood showed better light stability compared to untreated wood (Beckers *et al.* 1998). However, a UV absorber in the coating was needed to obtain good performance. Although treated wood showed some degradation at the surface resulting in a white to grey layer of loss cellulose fibres on the surface, untreated wood degraded into deeper layers of the wood. Application of a transparent topcoat on acetylated wood resulted in minimum colour changes. In outdoor exposure, blue stains attacked finished acetylated wood after a few months. Although the wood moisture content of acetylated wood is lower, blue stain appeared locally on all surfaces. An explanation for this might be the hygroscopicity of the coating itself leading to a high moisture content and thereby enhancing blue stain growth.

## CONCLUSIONS

The outdoor performance of paints was positively affected by both thermal and chemical (acetylation) modification of wood (*pinus radiata* and Scots pine sapwood). For thermally treated wood, the results were less pronounced than for acetylated wood. Outdoor exposure showed the same results as artificial weathering: cracking and flaking was strongly reduced. This was mainly caused by improved dimensional stability. Modification of the wood reduced stress applied to the coating: less swelling and shrinkage was observed. Therefore, the water borne coating showed less failure due to its maintained flexibility at low stress. The solvent borne coatings performed well on modified wood: due to its continuous cross-linking by oxidative drying, the coating becomes less and less flexible. Less stress from the substrate resulted therefore in fewer cracks. Ongoing cracking resulted in flaking of the paint from the wood. Artificially applied hail damage to a coating did not lead to a significant increase of cracking of the coating on either untreated or acetylated wood.

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## Dimensional Stability and Dynamic Viscoelastic Property of Wood Acetylated with Acetic Anhydride Solution of Glucose Pentaacetate

Eiichi Obataya<sup>1</sup>, Joseph Gril<sup>1</sup>, Yuzo Furuta<sup>2</sup>

<sup>1</sup> Laboratoire de Mécanique et Génie Civil, Université Montpellier 2

CC48, Pl.E.Bataillon 34095 Montpellier CDX 5, France

obataya@imgc.univ-montp2.fr

<sup>2</sup> Kyoto Prefectural University, Sakyo-ku Shimogamo, Kyoto 606-8522, Japan

furuta@kpu.ac.jp

**Keywords:** acetylation, glucose pentaacetate, dimensional stability, viscoelastic property, softening temperature, plasticization

### ABSTRACT

Spruce wood specimens were acetylated with a 3-15% acetic anhydride (AA) solution of glucose pentaacetate (GPA) at 120°C for 8hrs, and their dimensional stability and viscoelastic property were compared to those of the untreated and normally acetylated ones. The GPA was certainly introduced into the wood cell wall during the acetylation and it gave higher dimensional stability. At room temperature, the dynamic Young's modulus ( $E'$ ) of wood along the radial direction was enhanced by 10% with the introduction of GPA, while its mechanical loss tangent ( $\delta$ ) remained unchanged. These changes indicated the anti-plasticising effect of GPA molecules in the wood cell wall. On heating in the absence of moisture, the GPA-acetylated wood exhibited a marked drop in  $E'$  and a clear  $\delta$  peak above 150°C, whereas the  $E'$  and  $\delta$  of the untreated wood were quite stable up to 200°C during the measurement. The remarkable thermal softening of the GPA-acetylated wood was attributed to that of wood components plasticised with GPA.

### INTRODUCTION

Acetylation is an excellent method to improve the dimensional stability and durability of wood. The performance of the acetylated wood depends on the hydrophobic and bulky nature of the acetyl groups introduced into the amorphous regions of the wood cell wall (Rowell 1984). Although many attempts have been made for more effective acetylation with various catalysts and solvents, it is difficult to replace all of the cell wall intermolecular space with the acetyl groups. Thus the dimensional stability of the acetylated wood is naturally limited.

On the other hand, the dimensional stability of wood can be much improved by impregnation treatments. When the wood cell wall is previously swollen with wax, sugars and salts, it can hardly swell with moisture adsorption. In most cases, however, the impregnating substances are deliquescent and water-soluble. This is a problem when the treated wood is used in humid or wet conditions (Stamm 1983).

If some hydrophobic substance is introduced into the wood cell wall during the acetylation, the dimensional stability of the acetylated wood must be improved by the bulking effect of the impregnating substance without complicated procedures and severe treating conditions. In this respect, we tried to introduce glucose pentaacetate (GPA, see Fig.1) into the wood cell wall from its acetic anhydride (AA) solution. By using 5-20% GPA/AA solution instead of AA, the anti-



swelling efficiency (*ASE*) of the acetylated wood was enhanced by 10-30% with the penetration of GPA into the wood cell wall. The hygroscopicity of wood was reduced especially in highly humid conditions, and the bulking effect of GPA was not lost even by boiling in water because of its hydrophobic nature (Obataya *et al.* 2002).

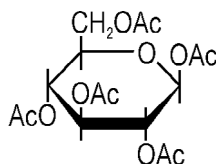


Figure 1 : Glucose pentaacetate (GPA)

In general, the wood is plasticised and softened when it is swollen with flexible, hydrophilic and/or low molecular weight substances. By acetylation, however, the dynamic Young's modulus of wood does not remarkably decrease and its mechanical damping remains almost unchanged, in spite of marked swelling due to the introduction of acetyl groups (Obataya *et al.* 2001). This fact can be explained by an anti-plasticising effect of the bulky and hydrophobic acetyl groups introduced. Since the GPA molecule is also bulky and hydrophobic, it might act as an anti-plasticiser in the wood cell wall at room temperature. On the other hand, it should be remembered that the GPA has melting points ranging from 110 to 130°C. Above these temperatures, the GPA might act as a plasticiser in the wood cell wall to reduce the softening temperature of the acetylated wood.

This paper describes the dimensional stability and dynamic viscoelastic property of the GPA-acetylated wood at various moisture conditions and temperatures, to show the plasticizing and anti-plasticizing effects of GPA in the wood cell wall.

## EXPERIMENTAL METHODS

### *Acetylation and hygroscopicity measurement*

Sitka spruce (*Picea Sitchensis*) wood specimens of 1cm (L, longitudinal direction) by 3cm (R, radial direction) by 3cm (T, tangential direction) were previously soaked in water for a week to remove the water-soluble extractives, and absolutely dried *in vacuo* at room temperature. The density ( $\rho$ ) of specimens was  $0.34 \pm 0.01 \text{ g/cm}^3$ . For the acetylation, acetic anhydride (AA, Wako Pure Chemical Inc.) and  $\alpha, \beta$ -D-glucose pentaacetate ( $\beta$  rich GPA, Pfanstiehl Labo.Inc.) were used. The dry specimens were soaked in 0, 3, 5, 10 and 15% GPA/AA overnight and subsequently heated in a separable flask at 120°C for 8 hours. The specimens were then immediately cooled at room temperature and dried *in vacuo* to remove the AA and acetic acid remaining there. Next, the specimens were dried completely at 105°C for 12 hours and heated at 160°C for 10 minutes. By this short *curing*, a part of GPA in the cell lumens penetrates into the cell wall without serious degradation of wood components (Obataya *et al.* 2002). Prior to the hygroscopicity measurement, the specimens were washed in water and absolutely dried *in vacuo*. The weight and dimensions of specimens were measured at 20°C and 11, 33, 57, 75, 92 and 97% relative humidities (*RH*). The specimens were finally soaked in water and boiled at around 95°C for an hour to measure their wet volume. Five specimens were used for each treating condition.

### *Viscoelastic measurement at room temperature*

Sitka spruce wood specimens of 1.5cm (L) by 12cm (R) by 0.3cm (T) were washed in water and dried completely *in vacuo*. At the first, the specimens were conditioned at 20°C and 33% *RH* for a month and their dynamic Young's modulus ( $E'$ ) and loss tangent ( $\delta$ ) along the R direction were

measured by using free-free flexural vibration method (Hearmon 1958). Next, thirty specimens with analogous  $\rho$  ( $0.46 \pm 0.03 \text{g/cm}^3$ ),  $E'$  ( $1.22 \pm 0.16 \text{GPa}$ ) and  $\delta$  ( $0.017 \pm 0.001$ ) were selected and divided into 6 groups. Of these, one group remained untreated and the other five were acetylated in the same manner as described above. All specimens were then dried *in vacuo* at room temperature, and their  $E'$  and  $\delta$  values were measured at 20°C and 0, 11, 33, 57, 75, 92 and 97%RH. The  $E'$  value was calculated from the  $\rho$  of specimen and its resonance frequency at the first mode vibration. The  $\delta$  was calculated from the half width of the resonance curve. The specimens and the equipments were settled in a closed box in which the RH was controlled with various aqueous salt solutions.

#### **Viscoelastic measurement at high temperatures**

Sitka spruce wood sheets of 10cm (L) by 6cm (R) by 0.07cm (T) were washed in water and acetylated with the same manner described above. The sheets were then cut into strips with a size of 4cm (R) by 0.4-0.5cm (L) and subjected to the following measurements: some specimens were absolutely dried *in vacuo* at room temperature, and their  $E'$  and  $\delta$  values along the R direction were measured in the temperature range from 20 to 200°C; the other specimens were soaked in water for a week and their  $E'$  and  $\delta$  values were measured in water over the temperature range from 5 to 100°C. Both these measurements were carried out using a viscoelastometer DMS 6100, Seiko Instruments Inc., equipped with a temperature controlled tube filled with dry air or water. The measuring frequency, programmed heating rate and the effective span of specimens were 5Hz, 2°C/min and 2cm, respectively.

## **RESULTS AND DISCUSSION**

#### **Dimensional stability of the GPA-acetylated wood**

Hereafter the acetylation with GPA/AA is described as "GPA-acetylation", being distinguished from the "normal" acetylation using AA. The weight percent gain (*WPG*) and volume percent gain (*VPG*) of acetylated wood specimens are listed in table 1. Since the *WPG* and *VPG* values did not strongly depend on the shape of specimen, here we describe the dimensional stability of the "block" specimens. The *VPG* of acetylated wood is plotted against the *WPG* in figure 2.

**Table 1: Weight percent gain (*WPG*) and volume percent gain (*VPG*) of spruce wood specimens due to the acetylation at 120 °C for 8 hours.**

Specimen	GPA/AA <sup>a</sup> [%]	<i>WPG</i> [%]			<i>VPG</i> [%]	
		Block <sup>b</sup>	Beam <sup>c</sup>	Sheet <sup>d</sup>	Block <sup>b</sup>	Beam <sup>c</sup>
Normal acetylation	0	23.6	25.3	20.4	7.8	8.2
	3	29.2	28.8	28.7	9.0	9.7
GPA-acetylation	5	30.6	32.0	30.5	10.6	11.1
	10	39.7	34.4	37.0	11.6	11.6
	15	49.3	41.5	51.1	11.8	12.8

<sup>a</sup>Concentration of GPA in GPA/AA solution used for the acetylation, <sup>b</sup>Specimens of 1cm (L) × 3cm (R) × 3cm (T), <sup>c</sup>Specimens of 1.5cm (L) × 12cm (R) × 0.3cm (T), <sup>d</sup>Specimens of 10cm (L) × 6cm (R) × 0.07cm (T).

Both the *WPG* and *VPG* increased with increasing GPA concentration. However, the *VPG* levelled off above 10%GPA/AA while the *WPG* increased almost linearly. This fact suggested that much of the GPA remained in the cell lumens at high GPA concentrations. Figure 3 shows the swelling in volume (*SV*) of the untreated and acetylated wood specimens plotted against the equilibrium moisture contents (*EMC*). The *SV* value is based on the volume of specimen in its untreated and absolutely dry state. Irrespective of treatments, the specimens swelled linearly with increasing *EMC* up to their fibre saturation points. By the acetylation, wood specimens were previously swollen with acetyl groups and GPA molecules introduced, while their maximum

volume remained almost unchanged. Consequently, the swelling due to moisture sorption was effectively reduced. The anti-swelling efficiency of the GPA acetylated wood ranged from 78 (3%GPA/AA) to 85% (15%GPA/AA) while that of the normally acetylated wood was 72%.

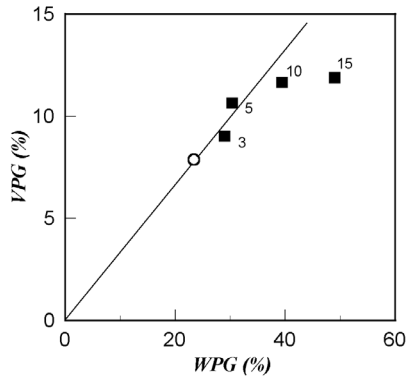


Figure 2: Plots of volume percent gain (VPG) vs. weight percent gain (WPG) due to normal acetylation (○) and GPA acetylation (■). Values beside plots indicate the GPA concentration used for the treatment.

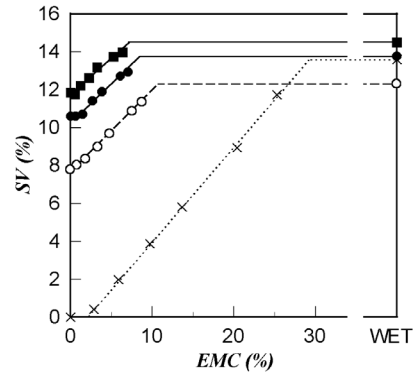


Figure 3: Swelling in volume (SV) of wood specimens plotted against equilibrium moisture content (EMC). ×, untreated; ○, acetylated with AA; ●, acetylated with 5%GPA/AA; ■, acetylated with 15%GPA/AA.

**Anti-plasticising effect of GPA at room temperature**

Figure 4a shows the  $E'$  and  $\delta$  values of the untreated and the acetylated wood specimens along the R direction at 20°C as a function of RH. Above 40%RH, the  $E'$  of the untreated wood decreased and its  $\tan\delta$  increased with an increase of RH. On the other hand, the  $E'$  and  $\delta$  values of the normally acetylated wood were quite stable against the RH change, because of remarkable reduction in the hygroscopicity. The effects of GPA-acetylation were qualitatively similar to those of the normal acetylation, but it should be noted that the  $E'$  values of GPA-acetylated woods were always higher than those of the untreated and the normally acetylated ones.

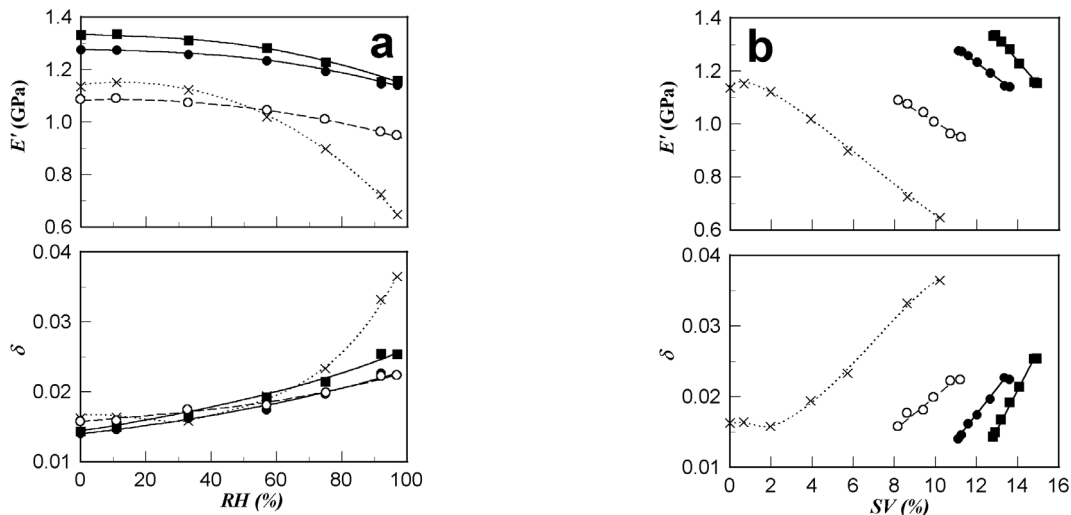
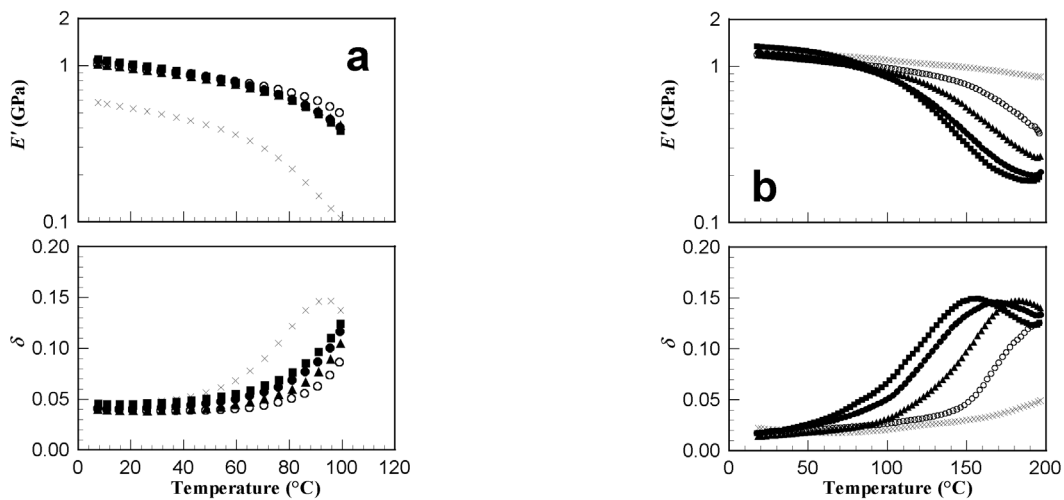


Figure 4: Dynamic Young's modulus ( $E'$ ) and mechanical loss tangent ( $\delta$ ) of untreated and acetylated wood specimens at 20°C as a function of RH (a) and SV (b). For keys, see Fig.3.

In figure 4b, the  $E'$  and  $\delta$  values of the untreated and the acetylated wood specimens are plotted against the SV. In general, water and various chemicals are introduced into the amorphous region of the wood cell wall. Since the amorphous region is viscoelastic and its Young's modulus is much lower than that of the crystalline region of the cellulose microfibrils, the swelling of wood

usually involves the reduction of  $E'$  and the increase of  $\delta$  unless a cross-linking structure is formed. However, as shown in Fig. 4b, the normally acetylated and the GPA-acetylated woods showed higher  $E'$  and lower  $\delta$  than the untreated one at the same  $SV$  level. Especially, the  $E'$  of the GPA-acetylated wood was about 10% higher than that of the normally acetylated ones in spite of remarkable swelling with the introduction of GPA. This fact suggested that the GPA acted as an anti-plasticiser in the wood cell wall, probably because of its bulky nature. Figure 5a shows the temperature variations of  $E'$  and  $\delta$  for the untreated and the acetylated wood specimens along the R direction in wet condition. The untreated wood exhibited a marked drop in  $E'$  and a clear  $\delta$  peak in the range from 60 to 100°C. This transition was attributed to the glass-rubber transition of lignin (Furuta *et al.* 2000). On the other hand, the  $E'$  of the acetylated wood decreased only slightly with increasing temperature, and its  $\delta$  showed no peak in the temperature range examined.



**Figure 5: Temperature variations of  $E'$  and  $\delta$  at 5Hz for untreated and acetylated wood specimens in wet (a) and absolutely dry (b) conditions.  $\times$ , untreated;  $\circ$ , acetylated with AA;  $\blacktriangle$ , acetylated with 3%GPA/AA;  $\bullet$ , acetylated with 5%GPA/AA;  $\blacksquare$ , acetylated with 15%GPA/AA.**

Among major components of the wood cell wall, the lignin is greatly reactive during the acetylation (Ohkoshi and Kato 1997). After acetylation, there is less space for the water molecules involving the plasticization of lignin, and the mobility of lignin itself must be reduced by bulky acetyl groups. Thus the glass-rubber transition of lignin shifts to higher temperatures. These may be the reasons for stable viscoelastic profile of the acetylated wood in water. The changes in  $E'$  and  $\tan\delta$  of the GPA-acetylated wood were slightly larger than those of the normally acetylated one, but still smaller than those of the untreated one. It was considered that the anti-plasticising effect of GPA was maintained even in hot water for its hydrophobic nature.

#### **Plasticizing effect of GPA at high temperatures**

Figure 5b shows the temperature dependence of  $E'$  and  $\delta$  for the untreated and the acetylated wood specimens along the R direction in the absolutely dry condition. The  $E'$  and  $\delta$  of the untreated wood was stable on heating. Meanwhile the normally acetylated wood showed a marked drop in  $E'$  and steep rise in  $\delta$  above 150°C. These changes were not due to the thermal degradation of wood constituents but attributable to some transition of wood components, because the repeating measurements gave almost the same results. At room temperature, the amorphous wood constituents in glassy-state are not plasticised with the introduction of acetyl groups. However, the acetyl groups can act as an internal plasticiser at high temperatures where the amorphous molecules in the wood cell wall are enough mobile. Otherwise a part of hydrogen bonds between the amorphous molecules are severed with the introduction of acetyl groups, to

increase the mobility of amorphous molecules. By the GPA-acetylation, the softening temperature of wood was reduced remarkably. Since the GPA-acetylated wood showed no loss peak corresponding to the melting of GPA (110-130°C), that considerable softening was not due to the melting of GPA itself but to the softening of wood components plasticised with GPA. It should be noted that the  $\delta$  peak of the acetylated wood shifted smoothly with increasing the GPA content while keeping its magnitude. This fact indicated that the GPA and the acetylated wood components were well dissolved in each other *i.e.* the GPA worked well as a plasticiser in the wood cell wall. Wood materials are easily softened with moisture, but relatively stable on heating in the absence of moisture. On the contrary, the GPA-acetylated wood is stable under wet condition while it can be well softened on heating even in the absence of moisture. In fact, the dry GPA-acetylated wood ( $WPG=37\%$ ) showed 86% reduction in  $E'$  from 20°C to 195°C, whereas that of the normally acetylated wood was 65%, and dry untreated wood, 32%. In this point of view, the GPA-acetylation is an effective method to enhance the thermal plasticity of the acetylated wood while keeping its excellent anti-water property. We have so far employed only GPA for its availability and safety, but various hydrophobic substances other than GPA will also penetrate into the wood cell wall in the same manner. Such a combined method might be effective for further property enhancement of wood by the chemical modification.

## CONCLUSIONS

Spruce wood specimens were acetylated with acetic anhydride (AA) solution of glucose pentaacetate (GPA). By using GPA/AA solutions instead of AA, the dynamic Young's modulus of the acetylated wood increased by 10% while its mechanical loss tangent remained unchanged at room temperature. These changes were interpreted by the anti-plasticising effects of bulky GPA molecules introduced into the wood cell wall. On the other hand, the GPA-acetylated wood was well softened above 150°C even in the absence of moisture. It was suggested that the GPA molecules acted as a plasticiser in the wood cell wall above its melting point.

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## Colour Measurement as means of Quality Control of Thermally Treated Wood

Margareta Patzelt, Gerhard Emsenhuber, Robert Stingl

Institute of Wood Science and Technology, BOKU - University of Natural Resources and Applied Life Sciences, Vienna, Austria, patzelt@edv1.boku.ac.at

**Keywords:** quality control, thermal modification, colour change, spruce wood

### ABSTRACT

Controlling the quality of thermally modified wood for different purposes is one of the main challenges in the field of wood modification. The effect of different modification parameters such as temperature, pressure, modification period, moisture content and surrounding atmosphere on the colour of spruce wood (*Picea abies* (L.) [Karst.]) was investigated. Complementary tests about specific physical properties like weight loss, and dimensional stability were carried out. Analysis of data with reference to the relation between colour attributes (using L\*a\*b-system) and selected wood properties showed significant correlation especially between colour attributes hue and lightness and weight loss, which turned out to be the most influencing factor for both physical and chemical properties of thermally modified wood. Based on this knowledge a non-destructive controlling system for thermally modified wood might be developed, which can be compared to already existing grading systems concerning strength especially for the glue laminated timber production. In this case quality assessment should be made possible in order to guarantee wood properties for specific product requirements.

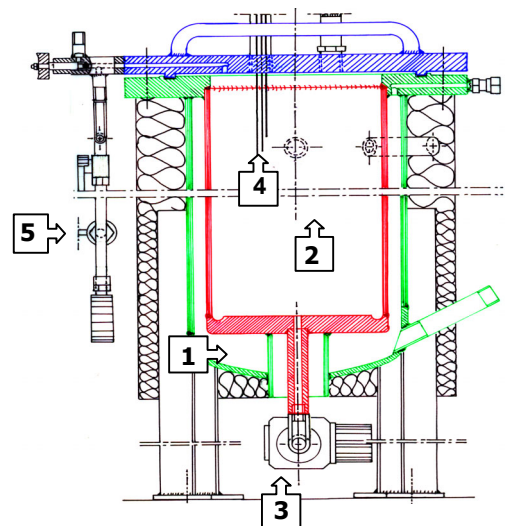
### EXPERIMENTAL METHODS

#### *Process equipment*

##### Vessel

Thermal treatment was carried out in a vertically arranged cylindrical pressure vessel (for laboratory use only) (figure 1). The design of heating system chosen was a hot steam stream evenly condensing at the outside of the jacket to obtain a consistent temperature distribution inside the vessel. The most process relevant features of the vessel are listed below:

- Maximum capacity reaction box: volume 0,01 m<sup>3</sup>
- Dimensions reaction box: height 0,45 m  
diameter 0,15 m
- Maximum pressure: 1 MPa
- Maximum temperature: 180° C



Legend:

- |                                   |                     |
|-----------------------------------|---------------------|
| 1 = Outside or hot steam range    | 4 = Thermocouple    |
| 2 = Reaction box                  | 5 = Pressure sensor |
| 3 = Valve for pressure limitation |                     |

Figure 1: Sectional drawing of the vessel

### **Colour measurement system**

The colour of the modified specimens was calculated with the Phyma CODEC 400. This two-beam spectral photometer with continuous illumination, responds in the range between 400 –and 700 nm (visible range). The light source used was a standard illumination D65 that serves for measurements at daylight conditions (6500 K colour temperature).

### **Thermal modification**

Spruce wood specimens for the following tests were thermally treated using one of the best documented processes, the moisture-heat-pressure method (Burmester 1973, Burmester and Wille 1976, Giebeler 1983, Tjeerdsma *et al.* 1998). The decomposition of wooden substances (expressed as loss of weight (LW) - table 1) is influenced by the following parameters:

- moisture content at the beginning of the process (oven dry up to fibre saturation)
- reaction temperature (132 - 165° C )
- reaction period (0 - 48 h)
- pressure inside the vessel (0,1 - 0,8 MPa)
- gaseous atmosphere (Nitrogen or air)

### **Loss of weight (LW)**

Loss of weight was calculated using following formula:

$$\text{loss of weight LW} = \frac{\left( \begin{array}{c} \text{oven dry mass} \\ \text{non modified wood} \end{array} \right) - \left( \begin{array}{c} \text{oven dry mass} \\ \text{modified wood} \end{array} \right)}{\left( \begin{array}{c} \text{oven dry mass} \\ \text{modified wood} \end{array} \right)} \quad (1)$$

### **Colour measurement**

The International Commission of Illumination (CIE) defined a colorimetric Standard which served as basis of the colour space system called L\*a\*b\* (CIELAB-System).

LCh is another way to define a colour in the LAB space using different terms. This system enables an independent assesment of 3 different colour parameters. Co-ordinate points are defined as: L = lightness or luminance relative to reference white; C = chroma, the distance from the central L axis or saturation relative to a reference white, h = hue, the angle referring to axis a (figure 2).

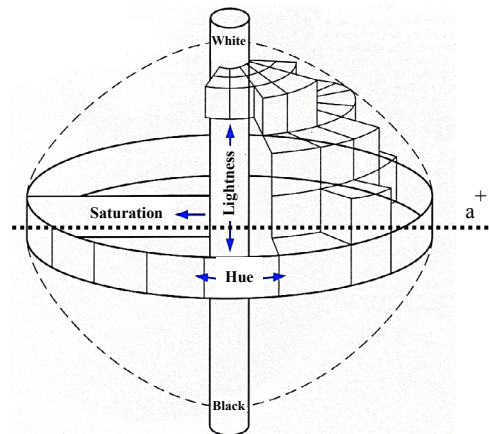


Figure 2: L C h- colour space system

### ***Selected wood properties of thermally treated wood (Adsorption and allowance for shrinking)***

With reference to ISO 12571 (2000) "Hygrothermal performance of building materials and products – Determination of hygroscopic sorption properties" the specimens were stored in different climate conditions. After standardised periods, the moisture content of the specimens was measured.

Based on EN 1910 (2000) "Wood and parquet flooring and wood panelling and cladding – determination of dimensional stability" the volume of the specimens stored in two different climate conditions was measured and allowance for shrinkage determined.

Table 1: Experiment variants of the moisture-heat-pressure method

	Moisture content [%]	Reaction-temperature [°C]	Reaction-period [h]	Pressure in the vessel [MPa]	Surrounding gaseous atmosphere	Loss of weight LW [%]
1	20	165	0	0,8	Nitrogen	0,46
2	20	130	24	0,8	Nitrogen	0,56
3	20	165	1,5	0,8	Nitrogen	1,02
4	20	165	3	0,8	Nitrogen	1,48
5	20	165	6	0,8	Nitrogen	1,98
6	0	165	24	0,8	Nitrogen	2,35
7	20	150	24	0,8	Nitrogen	2,41
8	20	165	24	0,1	Nitrogen	2,70
9	20	165	9	0,8	Nitrogen	2,95
10	20	165	12	0,8	Nitrogen	4,46
11	10	165	24	0,8	Nitrogen	4,80
12	20	165	18	0,8	Nitrogen	5,21
13	20	165	24	0,4	Nitrogen	5,68
14	20	165	24	0,8	Nitrogen	7,22
15	20	165	24	0,8	Air	9,17
16	30	165	24	0,8	Nitrogen	9,53
17	20	165	48	0,8	Nitrogen	9,99

## RESULTS AND DISCUSSION

At the start of the experiment, the colour of 384 non-treated spruce wood specimens was measured and gave the following result:

Table 2: Colour measurement of non-modified-wood

	Lightness L	Saturation C	Hue h
Non-modified-wood	91,30	19,05	84,58

One focus of interest was to find out, how changes of treatment parameters (Table 1) would affect lightness (L), hue (h) and loss of weight LW (1) of the specimens.

### Moisture content

Increased moisture content of the specimens was displayed in a reduced lightness of about 45% (significant correlation between moisture content and lightness:  $r=-0,828^{**}$ ) and a change of the hue from straw-yellow to orange-red. A linear dependence between loss of weight and moisture content could be observed. (figure 3).

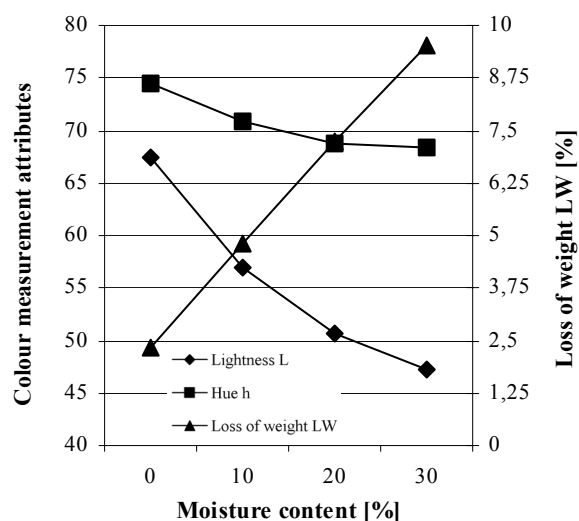


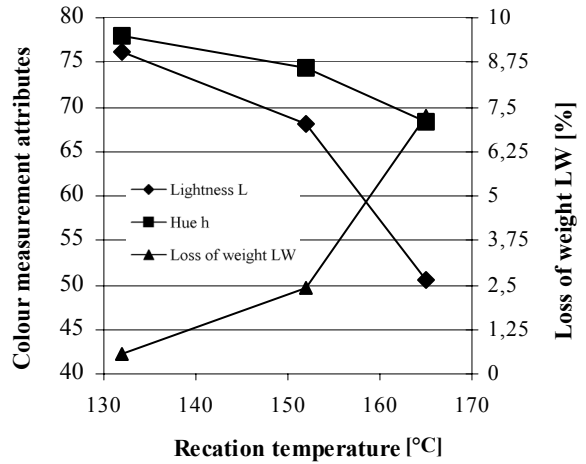
Figure 3: Relationship between moisture content, colour measurement attributes (lightness L, hue h) and loss of weight LW



**Reaction temperature**

Increasing temperature caused a decreasing lightness (about -40%), the angle shift of hue was about 10% (significant correlation between temperature and hue:  $r=-0,966^{**}$ ). Lower temperatures lead only to a slight loss of weight (figure 4). Above 150°C, a considerable increase in loss of weight could be observed (significant correlation between temperature and LW:  $r=0,950^{**}$ ).

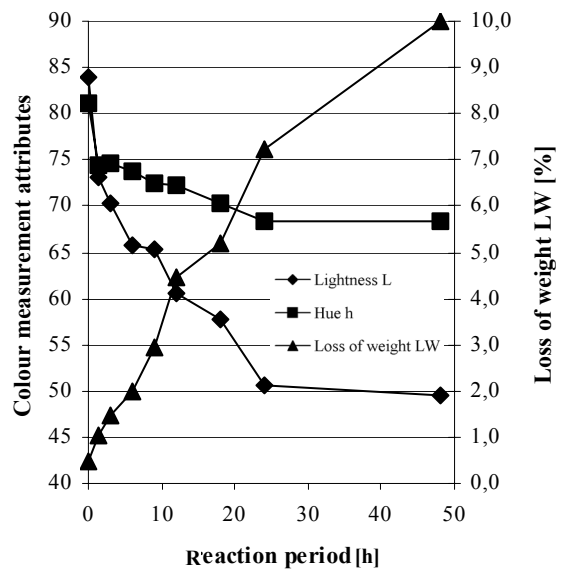
**Figure 4: Relation between reaction temperature, colour measurement attributes (L, h) and loss of weight LW**



**Reaction period**

As a result of the reaction period, the colour of the wood specimens became dark and changed from yellow to red hue (significant correlation between reaction period and hue:  $r=-0,727^{**}$ ). Similar to the colour change, the loss of weight LW increased with extended reaction period (figure 5).

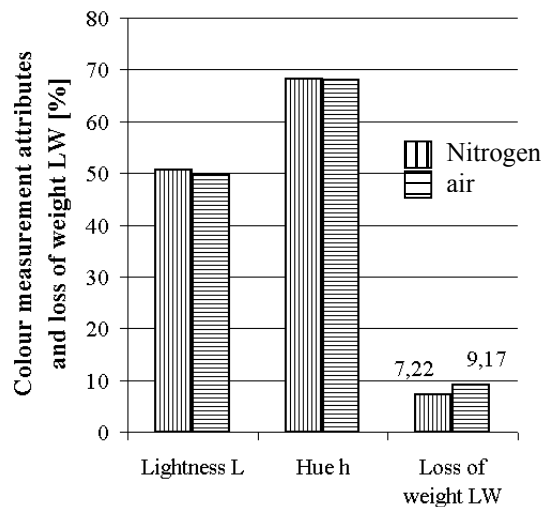
**Figure 5: Relation between reaction period, colour measurement attributes (lightness L, hue h) and loss of weight LW**



**Gaseous atmosphere**

In accordance to treatment parameters described previously, a change of the gaseous atmosphere has a significant impact on weight loss. In comparison to treatment in a Nitrogen atmosphere, loss of weight in an air atmosphere is higher (about 2%). Regarding the relationship between weight loss and colour parameters, in this specific case, no significant influence of surrounding atmosphere could be found. Colour attributes hue (h) and lightness (L) showed only insignificant differences (figure 6).

**Figure 6: Relationship between the parameters gaseous atmosphere (Nitrogen or air), colour measurement attributes (lightness L, hue h) and loss of weight LW**



Aiming at a colour based quality controlling system the correlation between colour parameters hue and lightness, loss of weight and selected properties of non modified and thermally treated specimens was studied. An obvious relationship between the colour attributes and the improved sorption properties can be seen (figure 7). Colour measurement seems to be a suitable method for controlling the properties of modified wood concerning dimensional stability.

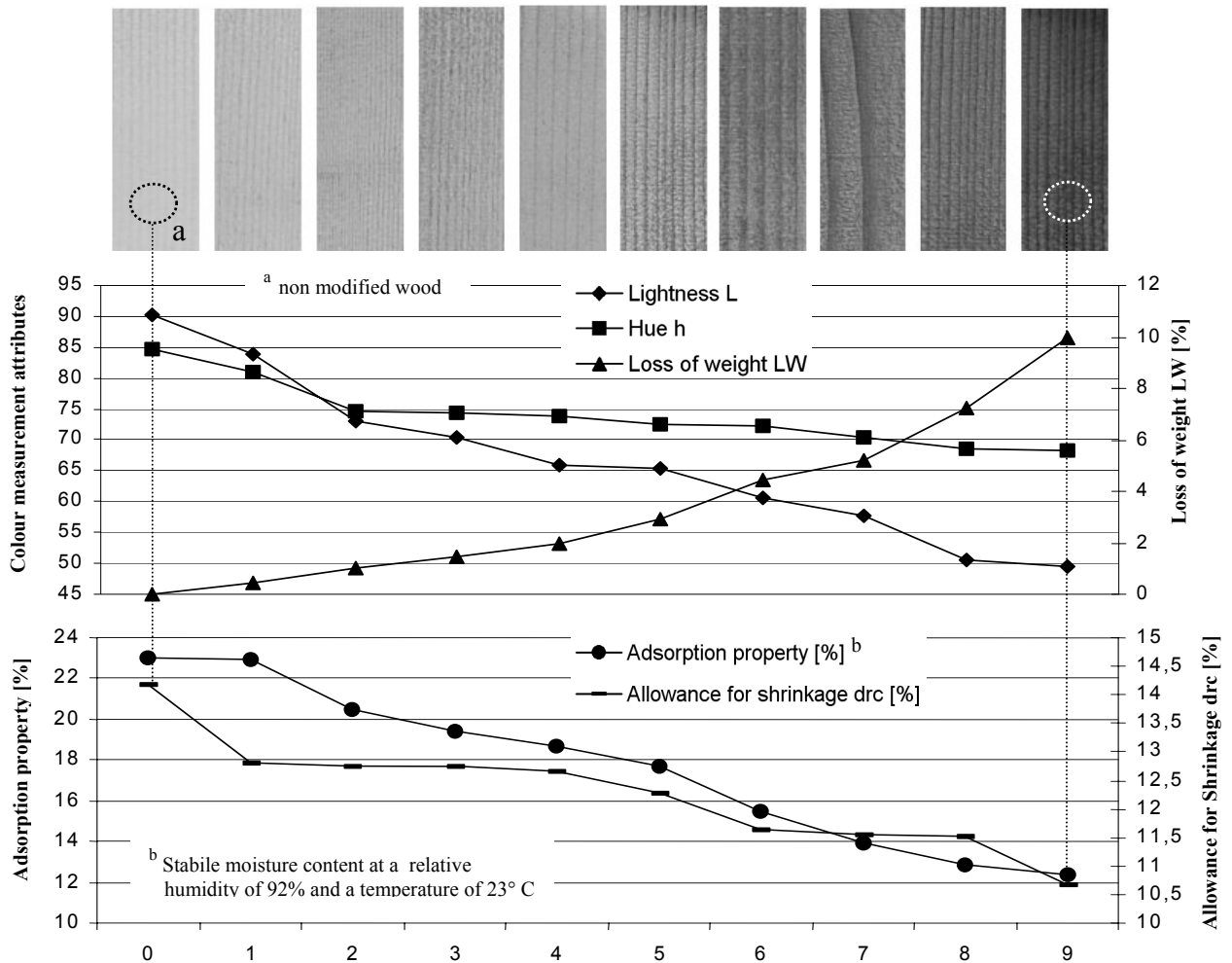


Figure 7: Relationship between colour measurement attributes (lightness L, hue h), loss of weight LW and selected wood properties (allowance for shrinkage resp. adsorption property)

## CONCLUSIONS AND OUTLOOK

This work shows a good correlation between time and temperature on the one side and the loss of weight on the other side. Further experiments (Patzelt *et al.* 2002) indicate that the loss of weight is the "main parameter" which influences the sorption properties. The actual quality and process optimisation of the industrial process for getting modified wood with set values for certain characteristics (*e.g.* sorption, swelling and shrinking), is made by controlling the reaction time and reaction temperature. The obtained experience shows, that this method is a good procedure to get reliable results.

The significant correlation between the colour attributes lightness and hue and the loss of weight of thermally modified wood (figures 3-6) should be able to serve as a base for a fast quality controlling system by an ordinary colour measurement system. A professional software tool for

such an application has the requirement to correlate the colour with the parameters described above (figure 7). It seems to be irrelevant in which way the weight loss of the modified wood is reached: High temperature and short reaction time lead to the same result in colour as lower temperatures and long reaction times. It should be taken into consideration that a colour based quality controlling system is only appropriate for selected wood properties.

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**(NEW) CHEMICALS**  
ORAL PRESENTATIONS



## Interactions between Wood and Melamine Resins - Effect on Dimensional Stability Properties and Fungal Attack

Irmgard Gsöls<sup>1</sup>, Manfred Rätzsch<sup>1</sup>, Christof Ladner<sup>2</sup>

<sup>1</sup>Kompetenzzentrum Holz GmbH (Wood K plus), St. Peter Straße 25, A-4021 Linz

i.gsoels@kplus-wood.at

<sup>2</sup>Institut für Forstentomologie, Forstpathologie, und Forstschutz an der Universität für Bodenkultur Wien, Billrothstraße 53/1/4, A-1190 Wien, Austria

**Keywords:** Norway spruce, melamine formaldehyde resin, modification, dimensional stability, fungi attack

### ABSTRACT

The effect of melamine formaldehyde resin modification of Norway spruce on dimensional stability and fungal attack was investigated. Wood was treated with resin solutions (5% to 30%) at 20 mbar and 25°C for 24 h, dried and cured. After 24 h water sorption, the swelling ( $S_{t,w}$ ) was reduced from 11% to 5% when a 30% solution was applied. While the dimensional stabilisation is independent of the hydrophobic properties of the resins, the effectiveness with which water sorption (WS) is reduced is strongly influenced by this parameter. Water sorption is reduced from 100% to 60% when a hydrophilic resin was used, and reduced from 100 % to 40 % when a hydrophobic resin was used for impregnation. Investigations on fungal resistance of modified Norway spruce showed that impregnation with melamine formaldehyde resins reduces fungal attack even at very low concentrations.

### INTRODUCTION

In 1964, Stamm described the suitability of melamine resins for dimensional stabilisation of wood. Inoue *et al.* (1993 a, b) examined physical properties of melamine resin-modified wood. The improved fungi resistance of such wood is well described, among others by Sailer (1995), Rapp and Peek (1996) and Rapp (1998). An extensive work on wood modification with melamine formaldehyde resins was published by Lukowsky (1999). Deka *et al.* (2000) demonstrated new aspects of wood treatment with thermosetting resins. It is well known that the efficiency of wood modification depends on the wood species. Spruce is difficult to modify, and literature on spruce wood modification is therefore rare. Since spruce is the major wood species in Austria, we investigated modification with melamine resins to reduce moisture sorption, to enhance dimensional stability, as well as to increase hardness and fungi resistance. In this paper, several aspects of dimensional stability and fungi attack are described.

### EXPERIMENTAL METHODS

#### **Wood sampling**

For our studies on dimensional stability, spruce wood (*Picea abies* (L.) Karst.) was cut into approximately 20 x 20 x 20 mm pieces from air-dried blocks. The samples were dried for 24 h at 103°C before impregnation. The density of the oven-dried pieces was 360 kg/m<sup>3</sup>.

For studies on fungal attack, spruce wood pieces measuring approximately 15 mm x 25 mm x 50 mm (tangential x radial x axial R/T 45°) were used according to EN 113. The samples were dried for 24 h at 103°C before impregnation. The density of the oven-dried samples was 460 kg/m<sup>3</sup>.

### **Resin treatment**

The applied resins and their properties are listed in Table 1.

*Table 1: Applied resins for impregnation*

Resin	Trade Name/Manufacturers	Properties	Molecular Weight
A	experimental product, AGROLINZ MELAMIN, AUSTRIA	fully methylated MFR, high NH content, 90% in butanol, pH = 8.5	M <sub>n</sub> = 700
B	Hilamin PA 43, DYNEA AUSTRIA	partially methylated MFR, high NH content, 72% in water, low molecular weight, pH = 8.5	M <sub>n</sub> = 600
C	experimental product, AGROLINZ MELAMIN, AUSTRIA	partially methylated MFR, high NH content, 25% in methanol/water, pH = 8.5	M <sub>n</sub> = 500

For fungal testing, resin C was diluted to 7.5% with methanol/water 1:1 w/w. For dimensional stability testing, resin A and resin B were diluted with methanol/water 1:1 w/w to the desired concentrations. The samples were placed in the impregnation solutions at room temperature. The vacuum impregnation procedure and curing conditions are shown in Table 2.

*Table 2: Treatment parameters*

Impregnation at room temperature	Drying and curing conditions
10 min at 20 mbar /10 min at 1 bar (5 circles)	72 h at room temperature
24 h at 20 mbar	24 h at 103°C
	1 h at 150°C

### **Test procedure**

#### **Dimensional stability**

For the determination of the moisture sorption (MS), the impregnated samples were stored for 7 days at 75% relative humidity and 25°C. The weight and dimensions before and after the 7 days were determined.

For the determination of the water sorption (WS), the impregnated samples were soaked in water for 24 h and the weight and dimensions before and after water sorption were determined. Moisture sorption (MS) and water sorption (WS) were calculated after Eq. 1

$$MS, WS = (W_{t,w} - W_t) \times 100 / W_t \quad (1)$$

where  $W_t$  is the weight of treated, oven-dried sample and  $W_{t,w}$  is the weight of the sample after moisture, resp. water sorption. The Volumetric swelling coefficient  $S_t$  ( $S_{t,m}$  after moisture sorption and  $S_{t,w}$  after water sorption) was calculated after Eq. 2.

$$S_{t,m}, S_{t,w} = (V_{w,t} - V_t) \times 100 / V_t \quad (2)$$

where  $V_{w,t}$  is the water-saturated volume of the treated wood and  $V_t$  is the oven-dried volume of the treated wood.

#### **Fungal attack**

The resistance against fungi was evaluated according to the standard EN 113 procedure. The samples were tested against 3 fungi: *Coniophora puteana* BAM 15, *Gloeophyllum trabeum* IFFF

691 and *Oligoporus placenta* f. *placenta* FPRL 280 (*Poria placenta*). Two treated samples and one untreated control were placed in one Kolle-Flask to obtain a direct comparison.

## RESULTS AND DISCUSSION

### *Dimensional stability*

The dimensional stabilities ( $S_{t,w}$ ) and the water sorption (WS) of melamine resin-treated samples after 24 h under water are shown in Tab. 3.

**Table 3: Swelling ( $S_{t,w}$ ) and water sorption (WS) of samples treated with a hydrophobic (A) and a hydrophilic (B) melamine formaldehyde resin (standard deviation in parentheses).**

Concentration of solution [%]	Resin A		Resin B	
	WS [%]	$S_{t,w}$ [%]	WS [%]	$S_{t,w}$ [%]
0 (control)	100 (7.5)	11.7 (0.01)	100 (4.1)	11.6 (0.10)
5	70 (1.6)	8.2 (0.46)	73 (2.4)	8.1 (0.67)
10	53 (4.8)	6.8 (0.68)	75 (0.9)	7.5 (0.72)
20	39 (5.4)	6.0 (0.48)	65 (4.0)	6.2 (0.37)
30	38 (7.2)	5.6 (0.31)	58 (5.1)	4.7 (1.2)

We found no significant differences in the dimensional stabilities ( $S_{t,w}$ ). Both resins reduced swelling by about 50% when a 30% solution was applied. The water sorption (WS) was reduced from 100% to 40% with resin A and from 100% to 60% with resin B. This significant difference might be a result of the more hydrophobic properties of resin A (see Table 1, resin properties). These results lead us to conclude that both resins form similar networks in wood during the curing reaction. The resins enclose the wood polymers, thus reducing swelling. Table 5 shows the dimensional stabilities ( $S_{t,m}$ ) and the moisture sorption (MS) of impregnated samples after 7 days at 75% relative humidity at 25°C.

**Table 5: Swelling ( $S_{t,m}$ ) and moisture sorption (MS) of samples treated with a hydrophobic (A) and a hydrophilic (B) melamine formaldehyde resin**

Concentration of solution [%]	Resin A		Resin B	
	$S_{t,m}$	MS	$S_{t,m}$	MS
0 (control)	9.2	15.8	9.0	14.4
3.6	7.8	14.8	7.8	12.8
7.2	6.8	13.2	7.2	12.1
10.8	6.2	12.1	7.2	11.4

In this case, resin impregnation apparently does not prevent moisture sorption by wood very well. One explanation for these results might be that, after 24 h water sorption, the equilibrium water content is not reached and the resins only delay the water sorption. Additional long-term experiments will be necessary to clarify the issue of melamine resin modification of Norway spruce.

### *Fungal attack*

Fig. 1 shows the mean percentage mass loss of resin C-treated samples based on the oven-dried mass of the impregnated wood. The WPG of the samples was 5.5 (standard deviation 2.5).



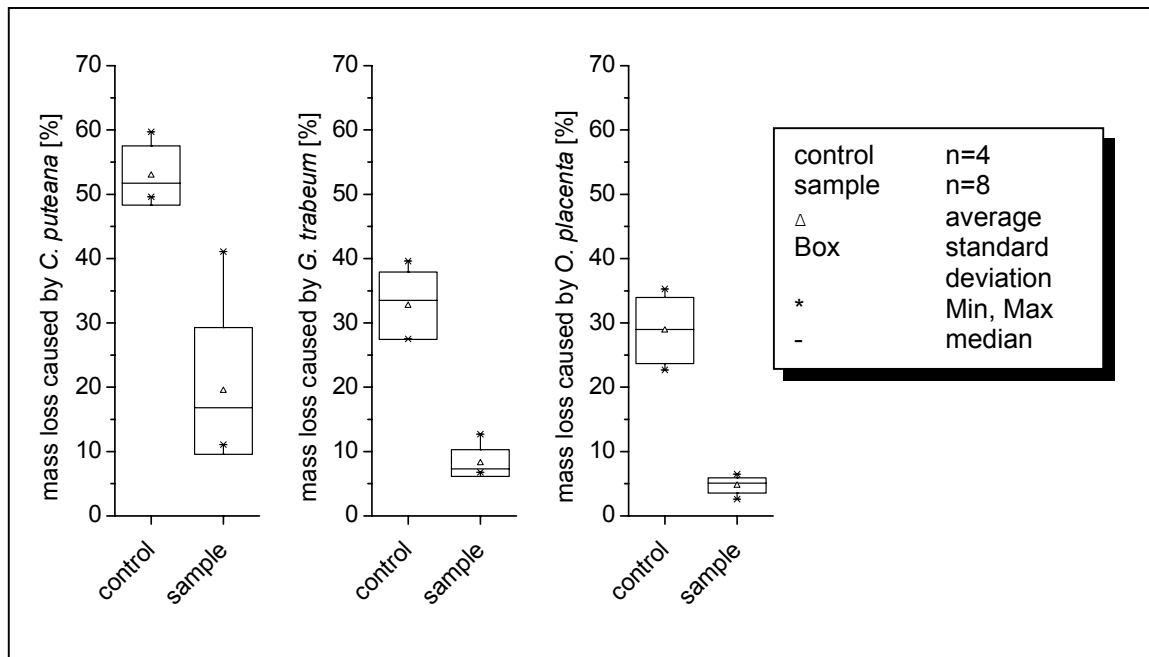


Figure 1: Mass loss of samples after 16 weeks using the fungi *C. puteana*, *G. trabeum* and *O. placenta*.

We found a significant difference between the mass loss of untreated Norway spruce and melamine formaldehyde resin-impregnated Norway spruce. The brown rot fungi *Coniophora puteana* caused a mass loss of more than 50 % on the Norway spruce controls. Treatment with 7.5 % melamine resin solution reduced the mass loss to 20 %. Lower mass losses were recorded for *Gloeophyllum trabeum* and *Oligoporus placenta* f. *placenta*. Untreated spruce showed mass loss of about 30%, whereas the impregnated samples showed 5% to 10%. These results were quite surprising because it is well known that spruce wood is difficult to impregnate and the resin concentrations in the samples were small (WPG 5.5%). The moisture contents of the samples after 16 weeks are listed in Table. 6.

Table 6: Moisture content of Norway spruce samples after 16 weeks

<i>C. puteana</i>		<i>G. trabeum</i>		<i>O. placenta</i>	
moisture content [%]		moisture content [%]		moisture content [%]	
control	sample	control	sample	control	sample
24.7	22.6	28.0	29.9	66.7	59.3
	34.4		28.5		60.5
26.5	26.0	36.4	43.7	56.8	33.8
	30.9		30.2		54.7
71.5	27.3	25.5	32.4	38.9	35.9
	31.8		21.7		36.8
31.2	41.6	29.3	25.5	42.8	69.8
	34.4		40.9		27.1

Clearly, the moisture content of the resin-impregnated samples and the control samples do not differ significantly. Thus, reduction of the moisture content can be excluded as an explanation for the higher fungi resistance of impregnated wood. The accessibility of the wood polymers probably plays an important role.

## CONCLUSIONS

Modification of Norway spruce wood with melamine formaldehyde resins increases dimensional stability. While the dimensional stabilisation is independent of the hydrophobic properties of the resins, the effectiveness with which water sorption is reduced is strongly influenced by this parameter. We assume that the resins enclose the wood polymers and that all of the investigated resins form similar networks in wood. Investigations on fungal resistance showed that impregnation with melamine formaldehyde resins reduces fungal attack even at very low concentrations. The moisture content during fungal attack is not the reason for this reduction. The most likely explanation is that the accessibility of the wood polymers is restricted and that this reduced accessibility plays an important role in fungi attack.

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## Improvement of Wood Properties by Treatments with Polyglycerol Derivatives

Patrice Soulounganga<sup>1</sup>, Cécile Roussel<sup>1</sup>, Bernard Loubinoux<sup>1</sup>, Edmond Wozniak<sup>2</sup>, Alain Lemor<sup>3</sup>, Philippe Gérardin<sup>1</sup>

<sup>1</sup> LERMAB, UMR INRA/ENGREF/UHP n° 1093, Equipe de Chimie Organique et Microbiologie, Université Henri Poincaré Nancy-1, Faculté des Sciences et Techniques,

BP 239, 54506 Vandoeuvre-les-Nancy cédex, France

<sup>2</sup> Xylochimie-Dyrupe, Site Industriel St-Antoine, 81030 Albi cédex, France

<sup>3</sup> Novance, BP 629, 60206 Compiègne, France

**Keywords:** polyglycerol, polyol, glyoxal, maleic anhydride, glycidyl methacrylate, wood, chemical modification, dimensional stabilisation, fungi

### ABSTRACT

The aim of this study is to develop new methods to improve wood properties based on the use of polyglycerol (PG) or polyglycerol derivatives due to the strong similarities of these products with polyethyleneglycols widely used in this area. Several solutions were investigated in this context. The first consists in the use of polyglycerol alone or fatty acid esters of PG. The results obtained indicated that polyglycerol are able to bulk the cell wood structure stabilizing thus the material, but are too leachable for outdoor applications. Fatty acid esters of PG are more resistant to leaching but confer poor stabilisation. A second approach concerns the formation of a polymeric network in wood obtained from PG, glyoxal with or without boric acid. Such a combination allows to stabilize wood dimensionally, to limit the depletion of boron and to protect wood against fungi. The third approach concerns the use of prepolymers obtained from polyglycerol and maleic anhydride, which are impregnated in wood and subject to *in situ* polymerisation. Finally, the last solution developed involves the use of polyglycerol methacrylate, easily obtained from polyglycerol and glycidyl methacrylate. Water-borne treatment of wood leads, after drying, to the formation of a polymer insoluble in water able to improve dimensional stability of wood but also its resistance to basidiomycetes.

### INTRODUCTION

Conventional wood preservation systems involve impregnation of broadly active biocides into the wood generating important environmental hazards, which may limit their scope of application in the future (Barnes and Murphy 1995, Suttie 1997). The environmental awareness of recent years has led though to an increased pressure on the use of preservative treated timber which justify investigations for novel wood preservation systems. An alternative preservation technique involves the formation of wood polymer composites which increase wood's dimensional stability, limit the access of water preventing thus fungal biodegradation (Fujimara *et al.* 1990, Doss *et al.* 1991, Nakano 1993, Schneider 1994, Yasuda and Minato 1995). Such techniques present the advantages of not introducing toxic chemicals into the wood, avoiding leaching of toxic substances in the environment.

A number of wood-polymer composites have been investigated to improve the dimensional stability of wood. They involve either the bulking of wood cell walls with various chemicals and/or the filling of the wood lumen by impregnation and polymerisation of vinyl monomers

limiting liquid or vapour water diffusion (Meyer 1984). Impregnation of wood with polyethyleneglycols (PEG) in water is probably one of the most known treatment for wood dimensional stabilisation (Stamm 1959, 1964, 1968). PEGs prevent cracking and checking of wood when the material is submitted to changing humidity. Valuable art carvings have been preserved in this manner and PEG treatment has permitted marine archaeologists to preserve water logged wooden ships brought up from lakes or oceans (Rowell 1984, Hoffmann 1986, 1988). However, PEG is rapidly leached out from the wood with water and is therefore inappropriate for out-door applications.

Polyglycerols (PGs), easily obtained from glycerine produced throughout the world from animals fats and vegetable oils, are polyethers presenting several similarities with polyethyleneglycols. Moreover they possess numerous hydroxyl groups, which permit to envisage the formation of a tridimensional network linked or not with wood decreasing their leachability. The aim of this paper is to describe our research carried out during the last few years to develop new wood dimensional stabilisation methods based on the use of polyglycerol derivatives.

## EXPERIMENTAL METHODS

### *Materials*

All commercially available chemicals, maleic anhydride (MA), glyoxal aqueous solution (GLX), glycidyl methacrylate (GMA), methyl ethyl ketone peroxide (MEKP) and cobalt naphtenate were purchased from Fluka-Sigma-Aldrich Chimie SARL (St Quentin Fallavier, France). Polyglycerol (PG3) was obtained from Novance (Compiègne, France) as a mixture of compounds with an average molecular weight of 242 ( $n \sim 3$ ). For some experiments, PG10 also obtained from Novance, was used.

### *Instruments*

$^1\text{H}$  NMR spectra were recorded in water on a Bruker AM 400 spectrometer. Solid state CP/MAS (cross-polarisation/magic angle spinning)  $^{13}\text{C}$  NMR spectra were recorded on a Bruker MSL 300 spectrometer at a frequency of 75.47 MHz. Chemical shifts were calculated relative to TMS. Acquisition time is of 0.026 s with number of transients of about 1200. All the spectra are run with a relaxation delay of 5 s, CP time of 1 ms and spectral width of 20 000 Hz. Spinning rates are 3.5 KHz. Chemical shifts are expressed in parts per million. IR spectra were recorded as thin films between NaCl plates or KBr disks on a Perkin Elmer FTIR spectrometer SPECTRUM 2000.

### *Synthesis of polyglycerol/maleic anhydride adduct (PG/MA adduct)*

Polyglycerol was mixed with 2 equivalents of finely powdered maleic anhydride and heated at 80°C for 3 hours. After disappearance of the IR absorption band of anhydride and appearance of a characteristic band corresponding to ester formed the reaction was cooled to room temperature and the product used without further purification.  $^1\text{H}$  NMR (DMSO  $\text{D}_6$ ): ( $\delta$ ): 3.2-4.4 (m,  $-\text{CH}_2-$  and  $-\text{CH}_2-$ ), 4.2-5.1 (br m, OH), 6.2 (d,  $J = 7.5$  Hz,  $-\text{CH}=\text{C}$ ), 6.4 (d,  $J = 7.5$  Hz,  $-\text{CH}=\text{C}$ ). IR (NaCl disk): 3400  $\text{cm}^{-1}$  ( $\nu\text{OH}$ ), 1730  $\text{cm}^{-1}$  ( $\nu\text{C}=\text{O}$ ).

### *Synthesis of polyglycerol methacrylate (PGMA)*

Polyglycerol (30 g) was mixed with a mechanical stirrer in a 100 ml flask with dimethylamino pyridine (300 mg). The mixture was then heated at 70°C to decrease its viscosity and glycidyl methacrylate (35.2 g) added dropwise over 2 min. The reaction kept at the same temperature during 15 min, cooled to room temperature and the product used without further purification.  $^1\text{H}$

NMR (D<sub>2</sub>O): ( $\delta$ ) : 1.88 (s, allylic CH<sub>3</sub>), 3.35-4.20 (m, CH and CH<sub>2</sub>), 5.63 (s, vinylic CH), 6.06 (s, vinylic CH). IR (NaCl disk): 3400 cm<sup>-1</sup> ( $\nu$ OH), 1718 cm<sup>-1</sup> ( $\nu$ CO), 1635 cm<sup>-1</sup> ( $\nu$ C=C).

### **Chemical modification of blocks**

Different solutions were used to impregnate wood blocks :

- solutions of PG3 (10, 30, or 50% in mass) prepared in water,
- solutions of PG3 (10% in mass) and glyoxal (10% in mass) prepared in distilled water
- solutions of PG/MA adduct (10 or 30% in mass) prepared in water with addition of MEKP (2 % in mass) and cobalt naphthenate (2% in mass) just before use
- solutions of PGMA (10, 20, 30 or 50% in mass) prepared in water with addition of MEKP (2 % in mass) just before use.

Weighed ( $m_0$ ) oven-dried beech (*Fagus sylvatica*) and pine (*Pinus sylvestris*) blocks (15 x 20 x 50 mm, radial x tangential x longitudinal) were used throughout this study. Blocks were placed in a beaker inside a desiccator and a vacuum of 5 mbar was drawn for 15 min using a pump. Blocks were then covered with the impregnation solution and the pressure returned to atmospheric. After two hours of soaking, blocks were drained for 5 min and cured under different conditions according to the nature of the treatment. Weight percent gain (WPG) was calculated from the initial and treated oven-dried weight according to the formula (1), where  $m_0$  is the initial oven-dried weight of the sample and  $m_1$  the treated oven-dried weight.

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

### **Chemical leachability**

Leachability of impregnated chemicals was estimated with different methods.

Leachability of PG3 or PGMA impregnated blocks was determined by placing blocks in distilled water (20ml for each block) under agitation during different times (1 h, 2 h, 4 h, 8 h, 16 h and 48 h) with change of water between each time. The leached blocks were then dried at 80°C for 2 days ( $m_2$ ) and the weight gain calculated after leaching. Leachability of GLX/PG10 impregnated blocks was determined after 6 hours of leaching in water followed by drying and weight gain calculation. Leachability of PG/MA impregnated blocks was determined after Soxhlet extraction for 6 hours with ethanol followed by drying and weight gain calculation.

### **Anti-Swelling-Efficiency measurements**

Anti-Swelling-Efficiency (ASE) was determined by measuring the increase in volume of treated and untreated blocks subjected to humidification. The volumetric swelling coefficients were calculated according to the formula (2), where  $v_2$  is the volume of water saturated wood and  $v_0$  or  $v_1$  the volume of dry untreated or treated wood.

$$S (\%) = ((v_2 - v_{0 \text{ or } 1})/v_{0 \text{ or } 1}) \times 100 \quad (2)$$

The percentage of swelling was calculated from the wet and oven-dried volumes of treated and untreated blocks according to (3), where  $S_c$  is the volumetric swelling coefficient of unmodified samples and  $S_m$  the volumetric swelling coefficient of modified samples.

$$\text{ASE} (\%) = ((S_c - S_m)/S_c) \times 100 \quad (3)$$

Humidification was performed by different means according to treatment method. Treated blocks with PG3 or MPGA and their controls were placed in a climatic chamber WTB BINDER type KBF 115 at temperature of 25°C and an humidity of 95% RH for approximately 2 months. Blocks treated with GLX/PG10 mixture or PG/MA adducts were humidified according to the

water soaking procedure by immersion in distilled water (30 mbar during 30 min followed by return to atmospheric, five cycles during five days) (Rowell *et al.* 1986).

### Decay test

Weighed ( $m_0$ ) and oven-dried pine blocks (*Picea abies*) or beech blocks (*Fagus sylvatica*) (15 x 20 x 50 mm in radial, tangential and longitudinal directions) were used for biological evaluations. Treated (4 replicates) and untreated (4 replicates) pine blocks were placed in 11 culture bottles (2 treated and 2 untreated blocks in each bottle) on a traditional sterile culture medium prepared from malt (15 g), gelose (15 g) in one liter of distilled water, inoculated with *Poria placenta* and incubated at 25°C for 16 weeks. Treated blocks (4 replicates) were placed on the same medium at 25°C during the same time without fungi inoculation in order to calculate weight loss due to diffusion of the product in the medium. After incubation, the blocks were dried at 80°C and weighed. Weight loss was expressed as a percentage of the initial oven-dried weight of the sample according to formula (4), where  $m_0$  is the initial weight of the samples and  $m_1$  the corrected weight of the samples exposed to fungi.

$$WL (\%) = (m_0 - m_1)/m_0 \times 100 \quad (4)$$

The same procedure was employed on beech blocks using *Coriolus versicolor* instead of *Poria placenta* to evaluate the effectiveness of the treatment.

## RESULTS AND DISCUSSIONS

Our first experiments were made on the use of polyglycerol alone as wood stabilizing agent by analogies with works done on polyethyleneglycols. The results obtained are reported in table 1.

*Table 1: Impregnations of wood blocks with PG3 aqueous solutions*

Concentration	Species	WPG (%) <sup>a</sup>	ASE (%)	WPG (%) <sup>b</sup>
10%	Beech	10.5	60.5	3.0
30%	Beech	26.8	80.2	11.9
50%	Beech	37.5	79.7	8.2
10%	Pine	17.2	36.6	4.3
30%	Pine	54	53.1	-
50%	Pine	72.8	-	-

<sup>a</sup>Weight gain before leaching, <sup>b</sup>Weight gain after leaching

The high solubility of PG in water permits an efficient impregnation and swelling of the wood cell walls by the chemical. Weight gains are in direct connection with the concentration of the solution used for impregnation leading to important ASE values even at low concentration. Concentration of 30% in mass seems sufficient to obtain good dimensional stabilisation. Weight gains measured after leaching are smaller showing an important lixiviation incompatible with outdoor applications. Different solutions were then investigated to try to improve the retention of PG in wood. A first alternative concerns the use of fatty acid esters of PG. The results obtained indicated that these compounds are more resistant to leaching but confer poor dimensional stabilisation when used in hydrocarbon solvent like hexane or spirdane D60, while their solubility was too low for water-borne applications. A second approach is founded on the formation of a polymeric network in wood obtained from PG and glyoxal. Indeed, it has been reported that the use of mixtures of polyols and glyoxal are able to improve wood dimensional stability (Takafumi 1995, Nakano 1993). The results obtained are reported in table 2.

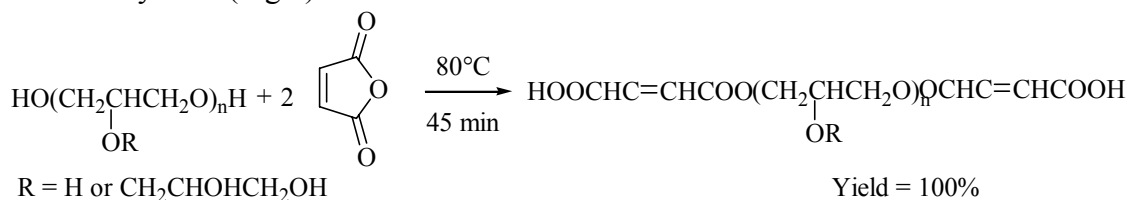
**Table 2: Impregnations of pine blocks with GLX/PG10 aqueous solutions with aluminium sulfate as catalyst**

Glyoxal (%)	PG10 (%)	WPG (%) <sup>a</sup>	WPG (%) <sup>b</sup>	ASE (%)	MOE (Mpa) <sup>c</sup>
10	10	25.1	16	63.5	18323 <sup>d</sup>
10	20	36.7	30	-	-
20	10	38.5	26.9	-	-
20	20	40	32.2	-	20926 <sup>d</sup>
0	0	-	-	-	7166

<sup>a</sup>Weight gain after 2 hours curing at 130°C without leaching, <sup>b</sup>Weight gain after 2 hours curing at 130°C followed by leaching, <sup>c</sup>Average value of 12 replicates, <sup>d</sup>After 4 hours curing at 100°C

Impregnation of pine blocks with aqueous mixtures of polyglycerol and glyoxal allows to obtain after curing at 130°C wood-polymer composites with improved dimensional stability. Determination of the modulus of elasticity indicates that the modified wood are more resistant to compression (compare 18323 or 20926 Mpa to 7166 Mpa). Addition of boric acid permits to obtain wood-polymer composites with improved dimensional stability but also with improved resistance to wood rotting fungi (Toussaint d'Auvergne *et al.* 2000). However in all cases, the chemical modification remain unstable to moisture and unappropriate for outdoor applications, which prompt us to investigate other alternatives.

For this purpose, we investigated the synthesis of vinylic derivatives of PG able to bulk the wood structure after water-borne treatment and to polymerise *in situ* avoiding leaching of the chemicals. First experiments were performed with PG/MA adducts obtained from polyglycerol and maleic anhydride (Fig 2).

**Figure 2: esterification of polyglycerols with maleic anhydride**

After preliminary studies on the conditions of polymerisation of PG/MA adducts (Roussel *et al.* 2001), we investigate their use for wood dimensional stabilisation using standard vacuum/pressure impregnation with different concentration (10 and 30% in water). After impregnation blocks were dried at 80°C during 3 days to estimate the quantity of chemicals in the wood. Half of the blocks were heated at 150°C during 45 min, while the other half was kept at 80°C. Blocks were finally weighed, subjected to Soxhlet extraction with ethanol (6 h) to remove unreacted chemicals, dried and reweighed (Table 3).

**Table 3: Impregnations of pine blocks with aqueous solutions of PG/MA adducts in the presence of MEKP (2%) and Cobalt naphthenate (2%)**

PG/MA (%)	WPG (%) <sup>a</sup>	Thermal treatment	WPG (%) <sup>b</sup>	WPG (%) <sup>c</sup>	ASE (%)
10	13.1	Yes	4.6	2	-
10	13.1	No	-	0	-
30	44.8	Yes	29.2	26.8	49
30	44.8	No	-	6.2	-
0	0	Yes	-	-	-

<sup>a</sup>Weight gain after drying at 80°C, <sup>b</sup>Weight gain after drying at 80°C followed by curing at 150°C during 45 minutes, <sup>c</sup>Weight gain after Soxhlet extraction with ethanol during 6 hours, <sup>d</sup>Average value of 12 replicates

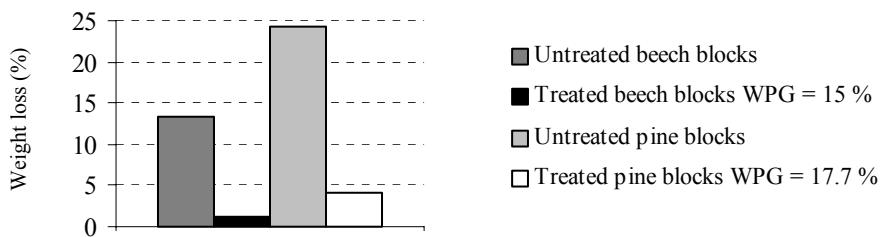


The tendencies observed during the polymerisation of PG/MA adducts impregnated in wood are similar to those observed for PG/MA alone. High temperature and free radical initiator are necessary to obtain a strongly reticulated polymer leading to satisfactory WPG after leaching. WPGs before and after thermal treatment at 150°C are different (compare WPG of 13.1 to 4.6 and 44.8 to 29.2) showing more pronounced dehydration due to loss of water (bonded water and/or esterification water). Anti-Swelling-Efficiency value of 49 % is obtained for blocks treated with 30 % aqueous solution of PG/MA adducts. This result is believed to be due to the restraint of swelling but also by the bulking effect of the treatment. Mechanical properties were then investigated on pine blocks impregnated with the same solution but heated at 100 or 150°C (Figure 3).



**Figure 3: Modulus of elasticity of untreated and treated with aqueous solution of PG/MA adduct (30 %) in the presence of MEKP (2 %) and cobalt naphthenate (2 %) pine blocks**

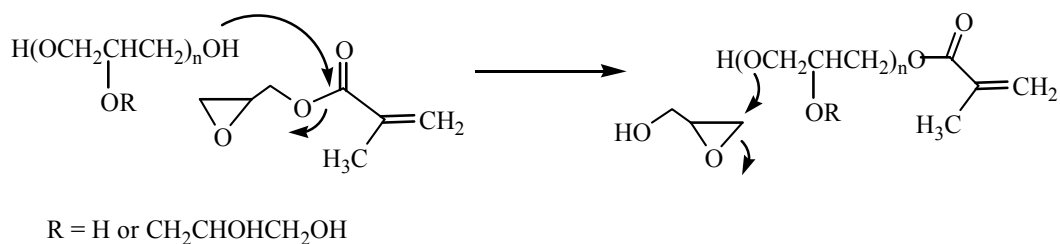
As expected, polymerisation of chemicals into the wood structure increases its resistance to deformation under load. Modulus of elasticity of treated wood are higher than those of untreated one, compare 20443 MPa or 17680 MPa to 7166 MPa, higher temperature leading to better results. Decay tests were performed on beech and pine blocks using respectively *Coriolus versicolor* and *Poria placenta*. The results are given in Figure 4.



**Figure 4: Weight loss after fungal attack of wood blocks treated with aqueous solution of PG/MA adduct (10 %) in the presence of MEKP (2 %) and cobalt naphthenate (2 %) heated at 150°C for 4 hours**

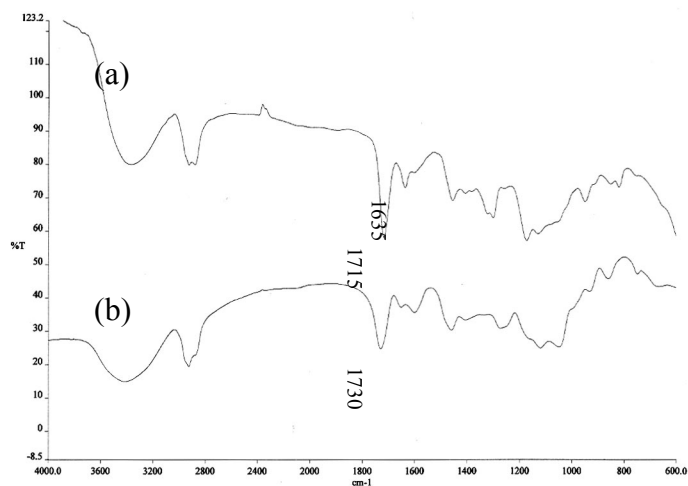
Chemical modification affords substantial bioprotection to beech blocks against *Coriolus versicolor*. Weight loss after 16 weeks of incubation is only of 1.1 % in treated samples, while weight loss in control samples is of 13.4 %. Sensibility of pine blocks to fungal attack caused by *Poria placenta* is greater compared to than of beech blocks to *Coriolus versicolor*. However, weight losses in control samples were considerably greater than in modified samples, 24.2 % compared to 4.2 %. These results demonstrated that appreciable wood protection occurred without using toxic chemicals.

The last approach envisaged concerns the use of polyglycerol methacrylate. Its synthesis was first investigated from methacrylic acid using standard esterification conditions. Several attempts made in toluene with 4-methoxyphenol or hydroquinone as radical scavenger which led systematically to polymethacrylic acid before any esterification reaction. Explanation of these failures is probably the poor solubility of polyglycerol in toluene. Other attempts using methacryloyl chloride in dichloromethane were also unsuccessful. Therefore, we investigated the reaction of polyglycerol with glycidyl methacrylate (GMA) by analogy with results concerning the synthesis of glycidyl methacrylate derivatised dextran (Van Dijk-Wolthuis *et al.* 1997). The reaction of polyglycerol with GMA occurs *via* transesterification of methacryloyl group yielding polyglycerol methacrylate and glycidol (Figure 5).



**Figure 5: Reaction of polyglycerol with glycidyl methacrylate**

Polyglycerol methacrylate polymerises rapidly using either UV activation (Morlat *et al.* 2001) or thermal activation in the presence of radical initiator as demonstrated by the displacement of the characteristic IR carbonyl band from 1715 to 1730 cm<sup>-1</sup> and the disappearance of the ethylenic band at 1635 cm<sup>-1</sup> (figure 6). <sup>13</sup>C MAS/CP NMR indicates also the polymerisation of polyglycerol methacrylate (non conjugated carbonyl signal at 178 ppm and no ethylenic signals) (figure 7).



**Figure 6: FTIR spectrum of polyglycerol methacrylate before (a) and after thermal treatment in the presence of MEKP (b)**

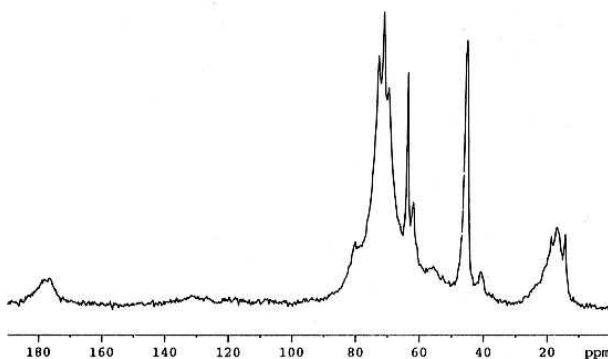


Figure 7:  $^{13}\text{C}$  CP/MAS NMR spectrum of polyglycerol polymethacrylate

Polyglycerol methacrylate was then investigated for wood treatment using standard vacuum/pressure impregnation. PGMA diluted in water (10, 20, 30 and 50 % in mass) in the presence of MEKP (2 % in mass) was impregnated in pine or beech blocks. After curing at 80°C during 3 days, blocks were subjected to anti swelling efficiency measurements. The results are given in Table 4.

Table 4: Impregnation of blocks with aqueous solutions of PGMA followed by heating at 80°C during 3 days<sup>a</sup>

Species	PGMA (%)	$m_0$ (g)	$m_1$ (g)	WPG (%) <sup>b</sup>	ASE (%)	WPG (%) <sup>c</sup>
Pine	10	7.92	8.81	11.22	29.47	5.98
Pine	20	8.39	10.66	27.39	55.48	11.07
Pine	30	10.02	13.29	32.69	47.79	25.22
Pine	50	8.88	14.58	65.38	63.41	56.41
Beech	10	12.27	13.55	10.47	6.61	6.69
Beech	20	14.10	16.18	14.75	28.27	10.41
Beech	30	14.47	17.67	22.14	20.90	16.92
Beech	50	13.87	18.35	32.54	48.36	19.70

<sup>a</sup> Average of 5 replicates, <sup>b</sup> Weight gain before leaching, <sup>c</sup> Weight gain after leaching

Weight gain and ASE are in direct connection with the amount of chemical used for impregnation. Dimensional stability of treated wood is considerably increased compared to untreated one. Level of polymerisation of PGMA was investigated after leaching of unreacted products. Indeed, polymerisation of PGMA carried out without solvent in the presence of MEKP leads to the formation of a water insoluble polymer, so that chemicals still present after leaching correspond principally to polymerisation products insoluble in water. Polymerisation increases with the concentration of PGMA used indicating that the dilution of PGMA into the wood is important for such type of treatments and particularly for their durability in outdoor application. Growth of *Poria placenta* or *Coriolus versicolor* on pine or beech blocks treated with PGMA is reported in Table 5.

**Table 5 : Weight loss of blocks treated with PGMA with or without addition of MMA exposed of fungal attack after 16 weeks**

Species	Treatment	Fungus	WG <sup>a</sup> (%)	WL <sup>a</sup> (%)
Beech	PGMA 10 % / MEKP 2 %	<i>Coriolus versicolor</i>	10.49 ± 0.34	5.00 ± 0.55
Beech	PGMA 20 % / MEKP 2 %	<i>Coriolus versicolor</i>	17.04 ± 1.92	5.28 ± 1.24
Beech	PGMA 30 % / MEKP 2 %	<i>Coriolus versicolor</i>	23.70 ± 2.41	2.20 ± 1.16
Beech	PGMA 50 % / MEKP 2 %	<i>Coriolus versicolor</i>	32.87 ± 8.42	4.43 ± 2.38
Beech	none	<i>Coriolus versicolor</i>	-	26.38 ± 5.21
Pine	PGMA 10 % / MEKP 2 %	<i>Poria placenta</i>	11.81 ± 1.51	4.45 ± 1.49
Pine	PGMA 20 % / MEKP 2 %	<i>Poria placenta</i>	27.31 ± 2.69	1.02 ± 0.55
Pine	PGMA 30 % / MEKP 2 %	<i>Poria placenta</i>	39.69 ± 7.21	4.67 ± 1.72
Pine	PGMA 50 % / MEKP 2 %	<i>Poria placenta</i>	73.25 ± 11.45	2.62 ± 2.13
Pine	none	<i>Poria placenta</i>	-	11.20 ± 6,63

<sup>a</sup> Average value of 4 replicates

In all cases, treated blocks are more resistant than untreated one. Weight losses are comprised between 2.2 and 5.2 % for white rot fungus and 0.7 and 4.4 % for brown rot fungi while controls show higher degradation (26.5 for white rot and 11.2 for brown rot).

## CONCLUSIONS

All these results demonstrate that polyglycerol derivatives are able to stabilize wood dimensionally and to protect it towards fungal attack. Among the different derivatives envisaged, it is very important to determine the performances of these latter ones compared to their technical and economical feasibility in order to envisage further developments. On these basis, polyglycerol, polyglycerol/maleic anhydride adducts and polyglycerol/glyoxal mixtures did not present the desired properties due to either important lechability or to high curing temperatures incompatible with further industrial investigations. Polyglycerol methacrylate appears as the most promising product for out-door wood dimensional stabilisation. It is easily synthesised starting from glycidyl methacrylate and polyglycerol without the use of any solvent. Soluble in water, it allows water-borne treatment. Polymerisation of PGMA can be achieved *in situ* after standard vacuum/pressure impregnation in the presence of MEKP by drying at low temperature. Modified blocks possess increased dimensional stability and are more resistant wood rotting fungi. Such wood polymer composite represents promising preservation method with environmentally and socially acceptable characteristics, which constitute a good alternative to highly toxic biocides used in this area today (Suttie 1997). The association of such treatments to biocides of class 3 could constitute interesting alternatives in the more or less long term to the use the products used currently in class 4.

## ACKNOWLEDGEMENTS

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## Modification of Wood with Silicon Compounds

Carsten Mai<sup>1</sup>, Steffen Donath<sup>2</sup>, Holger Militz<sup>3</sup>

<sup>1</sup> Institute of Wood Biology and Technology, Buesgenweg 4, 37077 Goettingen, Germany, cmai@gwdg.de; Phone: ++49-551-392051; Fax: ++49-551-399646

<sup>2</sup> Institute of Wood Biology and Technology, Buesgenweg 4, 37077 Goettingen, Germany, sdonath@gwdg.de; Phone: ++49-551-3919807; Fax: ++49-551-399646

<sup>3</sup> Institute of Wood Biology and Technology, Buesgenweg 4, 37077 Goettingen, Germany, hmilitz@gwdg.de; Phone: ++49-551-393541; Fax: ++49-551-399646

**Keywords:** silicofluorides, silicates, water glass, micro-emulsion, sol-gel process, organo-functional silanes

### ABSTRACT

Due to growing environmental concerns, the industry and research institutes are searching for new methods of wood preservation in order to substitute conventional preservatives, based on copper, chrome and arsenic or on creosotes. Chemical wood modification is a promising approach, not just to enhance the durability of wood, but also to improve further material properties. Among the variety of treatments described, various chemicals and formulations based on silicon compounds have been used. These treatments can be divided into the following systems:

- Fluorine containing compounds
- Inorganic silicates (“water glass”) and silicic acid condensates
- Wood-inorganic composites by sol-gel process
- Organo-functional silanes (sol-gel process)
- Micro-emulsion technology
- Chlorosilanes and trimethylsilyl derivatives
- Surface modification and hexamethyldisiloxane-plasma coating

The effects related to the various treatments vary from increase in dimensional stability, durability and fire resistance to enhanced hydrophobation of wood. In case of decay and fire resistance, a combination of silicon based systems with other chemicals was required to obtain satisfactory results. Due to the excellent water repellent ability and weathering stability of some treatments, an application of silicon treated wood under conditions of hazard class III (EN 335 outside above ground exposure) is recommended.

### INTRODUCTION

The modification of wood by the reaction with different chemicals aims to enhance various wood properties, such as durability against fungi and insects, physico-mechanical properties (dimensional stability, strength, hardness), stability towards UV-radiation and improvement of weathering performance, as well as fire resistance. A wide variety of silicon compounds have been applied for wood modification which required different treatment techniques and produced various changes of wood properties. Silicon which makes up about 25.8% of the earth's crust (Römpf 1995) is the second most abundant mineral after oxygen. It is naturally found in form of



mineral silicates (salts of silicic acid) which are mainly consist of polymeric  $\text{SiO}_2$  ( $m \text{SiO}_2 \cdot n \text{H}_2\text{O}$  or  $[\text{Si}(\text{OH})_4]$ ).

Elemental silicon shows a very low impact on animal organisms but as micro element it is required for the formation of bones and connective tissue. Silicates and most of the other silicon compounds are classified as non-toxic. However, dusts of quartz, cristobalite, tridymite, which contain  $\text{SiO}_2$  particles with a grain size of lower than  $5 \mu\text{m}$ , can cause a pneumoconiosis (silicosis) if inhaled over a long term (MAK  $0,15 \text{ mg/m}^3$ , Römpp 1995). A natural process of silicon treatment is the formation of silicified wood (Selmeier 1990, Furuno *et al.* 1986a, 1986b, 1988). Silicified wood develops during the burial of wood over millions of years through infiltration of silicic acid ( $\text{H}_4\text{SiO}_4$ ) into the wood tissue. A silica gel is formed by polycondensation, which further reacts to form quartz (chalcedone) and opal (wood opal). Compared to woods of temperate zones, many tropical woods contain a high percentage of silicon, which may exceed the content of calcium in certain species (Hillis and de Silva 1979). A correlation between the silica content and the resistance against marine borers of certain woods (*Dicorynia guaianensis*, *Syncarpia glomilifera*) could not be verified (De Silva and Hillis 1980). It is the aim of this article to describe and evaluate the various silicon based treatment systems and the resulting wood properties caused by the treatment.

#### **Fluorine containing compounds**

Various silicofluorides, *i.e.* salts of hexafluorosilicic acid (hydrofluorosilicic acid,  $\text{H}_2\text{SiF}_6$ ) have been proposed as wood preservatives (Broese van Groenou *et al.* 1952). Nowadays, commercial products are based almost exclusively on the zinc salt and the magnesium salt. For instance, in Germany at present, (Anonymous 2001) two products which contain 90.3% and 86.5% of magnesium silicofluoride, respectively, are registered. Both products are recommended for application in hazard classes 1 (EN 335; above ground, covered, dry) and 2 (EN 335, above ground, covered, risk of wetting). Silicofluorides are toxic. Since they do not react with the cell wall to form covalent bonds any positive effect on dimensional and weathering stability cannot be expected. A similar area of application has been described for Silafluofen, a silicon-containing organic insecticide against wood-boring insects and termites (Rustenburg and Klaver 1991, Adams *et al.* 1995, Nakayama *et al.* 2001).

#### **Water glass and silicic acid condensates**

Water glasses are potassium or sodium silicates or solutions thereof. A typical water glass is composed of 2 – 4 mol silicate and 1 mol alkali oxide. Due to hydrolysis, water glasses contain mainly hydrogen salts such as  $\text{M}_3\text{HSiO}_4$ ,  $\text{M}_2\text{H}_2\text{SiO}_4$ ,  $\text{MH}_3\text{SiO}_4$  (with  $\text{M} = \text{K}, \text{Na}$ ). In the pure state, water glasses are transparent and colourless, while technical products are bluish or greenish, due to iron impurities or yellowish to brown coloured glasses. At elevated temperature and pressure, water glasses are soluble in water and form a colloidal clear, heavily alkaline solution (pH higher than 12). The silicate can be precipitated from the solution by addition of acids, or of metal solutions. They are insoluble in cold water and are gradually decomposed by carbon dioxide from the air, leading to the formation of concentrated sols, gels or precipitations of silicic acid (Römpp 1995).

Treatment with aqueous water glass was conducted, either in a single step (Matthes *et al.* 2002), or in a two-step procedure (Furuno *et al.* 1991, 1992). In the first step, wood veneers were impregnated with sodium water glass solutions ( $\text{Na}_2\text{O} \cdot n \text{SiO}_2$ ,  $n = 2.06-2.31$ ). In a second step, the specimens were infiltrated with metal salt solutions, in order to precipitate the silicate within the wood structure by replacing sodium ions in water glass. Various salts such as aluminium sulphate ( $\text{Al}_2(\text{SO}_4)_3$ ), calcium chloride ( $\text{CaCl}_2$ ), barium chloride ( $\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$ ), boric acid ( $\text{H}_3\text{BO}_3$ ), borax ( $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$ ), boron trioxide ( $\text{B}_2\text{O}_3$ ), potassium borate ( $\text{K}_2\text{B}_4\text{O}_7 \cdot 4\text{H}_2\text{O}$ ) and ammonium borate ( $(\text{NH}_4)_2\text{O} \cdot 5\text{B}_2\text{O}_3 \cdot 8\text{H}_2\text{O}$ ) were tested (Furuno *et al.* 1992, 1993). The

impregnation of the hardwoods tested (hinoki, buna), resulted in a significantly higher WPG than that of the softwood (kaba). Electron probe x-ray microanalysis (EPMA) showed that the various adducts of silicates were located mainly in the cell lumina (Furuno *et al.* 1992). All impregnated wood specimens displayed strongly negative moisture excluding efficiencies (MEE), due to the high hygroscopicity of both the water glass and the un-reacted salts in the lumina of the cells. Leaching experiments revealed that considerable amounts of chemicals could be washed out from the specimens (Furuno *et al.* 1992, Matthes *et al.* 2002). This was partly circumvented by the soaking of water glass treated wood with aqueous acetic acid, prior to the second precipitation step (Furuno and Imamura 1998). Anti shrink efficiency (ASE) reported for the various treatments varied in a great deal (3-69% for  $\text{Al}_2(\text{SO}_4)_3$ ), although the bulking of samples displaying high ASE was rather small (Furuno *et al.* 1992).

All specimens treated in two steps, displayed a high fire resistance, except those that were treated with barium chloride in the second step (Furuno *et al.* 1991, 1992, 1993). Water glass treatment significantly reduced the bending strength, while the dynamic and static moduli of elasticity (MoE) were only slightly changed (Furuno *et al.* 1992). Strength properties were found to be dependent on the curing temperature after impregnation: on air drying (20°C) the strength of treated wood remained unchanged or slightly increased, while high temperature drying (103°C) brought about a significant strength reduction. This reduction was ascribed to the high pH of the wood, which resulted in a hydrolysis of the cell wall polysaccharides at elevated temperature (Matthes *et al.* 2002).

Fungal decay tests of water glass treated wood were difficult to conduct, due to high amounts of leaching chemicals (Furuno *et al.* 1991, 1992). In addition, the moisture content of wood blocks during fungal incubation (according to EN 113) was partly too high (Matthes *et al.* 2002). Decay resistance against the brown-rot fungus *Tyromyces palustris* and the white-rot fungus *Coriolus versicolor* revealed the highest protection by combined treatment of water glass and boron salts. Single treatment with boron salts (without water glass) or water glass (precipitated with acetic acid) caused lower durability (Furuno *et al.* 1991, 1992, 1993, Furuno and Imamura 1998). Wood treated with water glass alone (without precipitation) revealed a high decay-resistance (EN 113) both with and without leaching (EN 84) prior to the test (Matthes *et al.* 2002). The termite resistance of leached specimens was particularly enhanced in the samples treated with boric acid, borax and potassium borate combined with water glass. Single treated wood with these boron compounds showed 5-10 times higher weight losses (Furuno and Imamura 1998).

Water glass treatment was also combined with acetylation or propionylation (Li *et al.* 2000, 2001). While the ASE of double treated specimen was only slightly reduced compared to the esterified wood samples, the MEE significantly decreased. The whole treatment was recommended as flame-retarding due to an increased oxygen index.

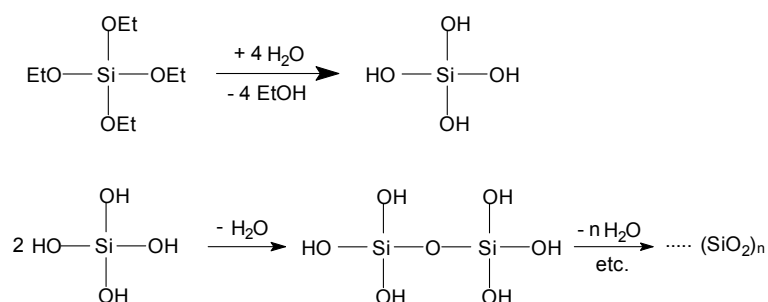
In a further approach, wood blocks were treated with gels of silicic acid. These gels were prepared by acidifying sodium silicate solution and colloidal silicic acid solution (CSAS). In addition, gels from a silicic acid monomer solution were prepared by ion exchange of sodium silicate (silicic acid monomer solution; SAMS; Yamaguchi 1994a, 1994b, 2001, 2002). Sugi wood blocks were vacuum impregnated with SAMS in concentrations of 5%, 7.4% or 10.7% as well as CSAS (30% colloidal silica). All wood properties reported were affected by the non-uniform distribution of the gel within the wood which was confirmed by x-ray mapping. Strength properties were not significantly improved except in case of treatment with 5% SAMS. The moisture excluding efficiency (MEE) and ASE at 100% r.h. were highest after treatment with 5% SAMS (about 40% and 20%, respectively); the values for ASE were in the same range as for tetraethoxysilane TEOS treated wood (see below; Saka *et al.* 1992). In all other cases the ASE

was below 20%. Wood treated with SAMS or CSAS did not show a higher decay resistance against brown-rot (*F. palustris*) than untreated wood. However, a combined treatment with iron, zinc, cobalt, copper or boric acid significantly reduced the weight loss, particularly with application of boric acid. The termite resistance (*Coptotermes formosanus*) of wood treated with CSAS or SAMS was only slightly higher than that of untreated wood, but could be significantly enhanced by a combination with boric acid or copper, respectively. Flame resistance was increased by CSAS treatment and was further enhanced on combination with boric acid (Yamaguchi 2001, 2002).

It is difficult to determine the number of commercially available wood preservatives which contain water glass or other silicates, since several formulations available on the market contain these compounds as additives in order to enhance certain properties. As an example a crucial contribution of water glass in a wood preservative formulation is described in the patent literature (Eck 2002). The role of water glass in the formulation is assumed to be the silification of wood, which seals the pores and prevents the recognition of the wood substrate by fungi or insects.

#### **Wood-inorganic composites by sol-gel process**

Wood modification applying the sol-gel process of silicon alkoxides has been reported by several research groups. The formation of inorganic gels can be divided in two stages (Fig. 1). In the first step the silicon alkoxide groups (silicic acid esters) are hydrolysed by water molecules to form siloxanes. In a subsequent step the siloxanes condense to polysiloxanes.



**Figure 1: Mechanism of the sol-gel process**

The application of the sol-gel process was most intensively studied by Saka *et al.* (2001). Wood veneers of hinoki were moisture conditioned and subsequently treated with an acidified alcoholic solution of alkoxysilanes. Tetra ethoxy silane (= tetraethyl orthosilicic acid; TEOS) was mainly tested for the experiments. X-ray mapping (SEM-EDX) showed that in the treated specimen, silicon was mainly located in the cell wall, while in specimens which were water saturated before incubation, the silicon was deposited in the cell lumina (Saka *et al.* 1992). No, or low ASE was observed when silicon compounds were mainly located in the lumina, while specimens which were fibre saturated before treatment showed a continuous increase of ASE up to 42% with increasing WPG (Ogiso and Saka 1993). The flammability of wood was significantly reduced by all treatments but the effect was more pronounced when silicon was incorporated in the cell wall rather than deposited in the lumina (Saka *et al.* 1992, Ogiso and Saka 1993). The fire resistance properties were enhanced by combination of TEOS with trimethylphosphite (TMP) and /or trimethylborate in order to produce  $\text{SiO}_2\text{-P}_2\text{O}_5\text{-B}_2\text{O}_3$  wood-inorganic composites (TMB; Miyafuji and Saka 1996, Saka *et al.* 2001).

Further fire resistant silicon oligomers with ethylphosphite and / or boric hydroxide residues were produced, that revealed higher resistance to leaching than the  $\text{SiO}_2\text{-P}_2\text{O}_5\text{-B}_2\text{O}_3$  compounds. Therefore, methyltrimethoxy-

silane were reacted with boric acid and subsequently triethylphosphite (TEP) or phosphoric acid were added. The resulting oligomers contained different proportions of silicon and phosphorous or boron, respectively, and were assumed to be siloxane tetramers (Miyafuji *et al.* 1998). For all boron adducts, leaching was significantly reduced when 2-heptadecafluorooctylethyltrimethoxysilane (HFOETMOS) was additionally applied in the impregnation. TEOS treated specimens showed a high resistance against termite attack (*Reticulitermes speratus*), especially when silicon was deposited in the cell wall (Ogiso and Saka 1993).

In a further approach, sols were prepared from TEOS prior to impregnation *i.e.* the hydrolysis and condensation were started outside the wood (Bücker *et al.* 2001, Reinsch *et al.* 2002). Degree of cross-linking of the polysiloxanes was controlled by the concentration of TEOS in ethanol and by other synthesis parameters, such as reaction time. The equilibrium moisture content (EMC) and water uptake in a dipping test were reduced, indicating good water repellence due to the silica gel. Bending strength was unchanged and the Young's modulus was slightly reduced by the treatment. Decay by the brown-rot fungus *Poria placenta* (EN 113) resulted in a weight loss between 12-16% in TEOS treated specimens (about 40% in untreated specimens). The test on the decay resistance against larvae of *Hylotrupes bajulus* according to EN 46 revealed that the larvae failed to attack TEOS treated wood (Reinsch *et al.* 2002).

A commercial application of gels based on TEOS for the treatment of wood is described in the patent literature (Böttcher *et al.* 2000). The durability was reportedly enhanced just initially because there has been a delay in the colonisation of impregnated wood but subsequently the decay proceeded with a similar velocity as in untreated wood (Scheithauer *et al.* 1998). Thus, gels produced by condensation of TEOS are applied as controlled release matrix for biocides such as boric acid (Böttcher *et al.* 1999). Specimens treated by dip coating (15 min) with the silica sol and boric acid combined did not show any mass loss in fungal (*Coniophora puteana* EN 113) and termite tests (*Reticulitermes santonensis*, EN 117). Treatment with TEOS (partly combined with CCA) caused an effective protection against marine boring teredinids but all tested timber species were attacked by the crustaceans *Limnoria* and *Sphaeroma*. *Pinus radiata* sapwood and *Corymbia maculate* natural rounds could be protected against teredinids while resistance of *Eucalyptus delegantensis* heartwood was not enhanced (Scown *et al.* 2001).

#### **Wood treatment with organo-functional silanes (sol-gel process)**

A variation of the sol-gel process which applies tetraalkoxysilanes and produces inorganic glasses consisting of pure polymeric SiO<sub>2</sub> is the use of organo-silanes (Fig. 2). These are bifunctional molecules which contain three silicon-functional alkoxy groups, mainly methoxy and ethoxy groups, and an organo-functional group, which increases e.g. the hydrophobicity of the gel or forms a covalent bond with the cell wall polymers. Organo-functional silanes were mainly applied in combination with TEOS or other gel forming precursors and impregnated in one step. Various property enhancers such as 3,3,3-trifluoropropyltrimethoxysilane (TFPTMOS), 2-heptadecafluorooctylethyltrimethoxysilane (HFOETMOS) and decyltrimethoxysilane (DTMOS, Fig. 2) were shown to prevent leaching from SiO<sub>2</sub>-P<sub>2</sub>O<sub>5</sub>-B<sub>2</sub>O<sub>3</sub> wood components due to hydrophobation (Saka and Tanno 1996). In a further study on SiO<sub>2</sub>-P<sub>2</sub>O<sub>5</sub>-B<sub>2</sub>O<sub>3</sub> wood components TEOS was compared to methyltrimethoxysilane (MTMOS, Fig. 2). The fire retarding properties in both systems were very similar but the leachability of the fire retardants was significantly lower at application of MTMOS. Several compounds known to improve fire resistance were tested in the TEOS and MTMOS system such as trimethylphosphite, diethylphosphite, terakis(hydroxymethyl)phosphonium chloride, phenylphosphonic dichloride and dimethylphenylphosphonate (Saka and Ueno 1997). Wood-inorganic Na<sub>2</sub>O-SiO<sub>2</sub> composites prepared by adding sodium methoxide or sodium acetate to the reaction system of MTMOS also revealed high fire resistance (Miyafuji and Saka 2001).

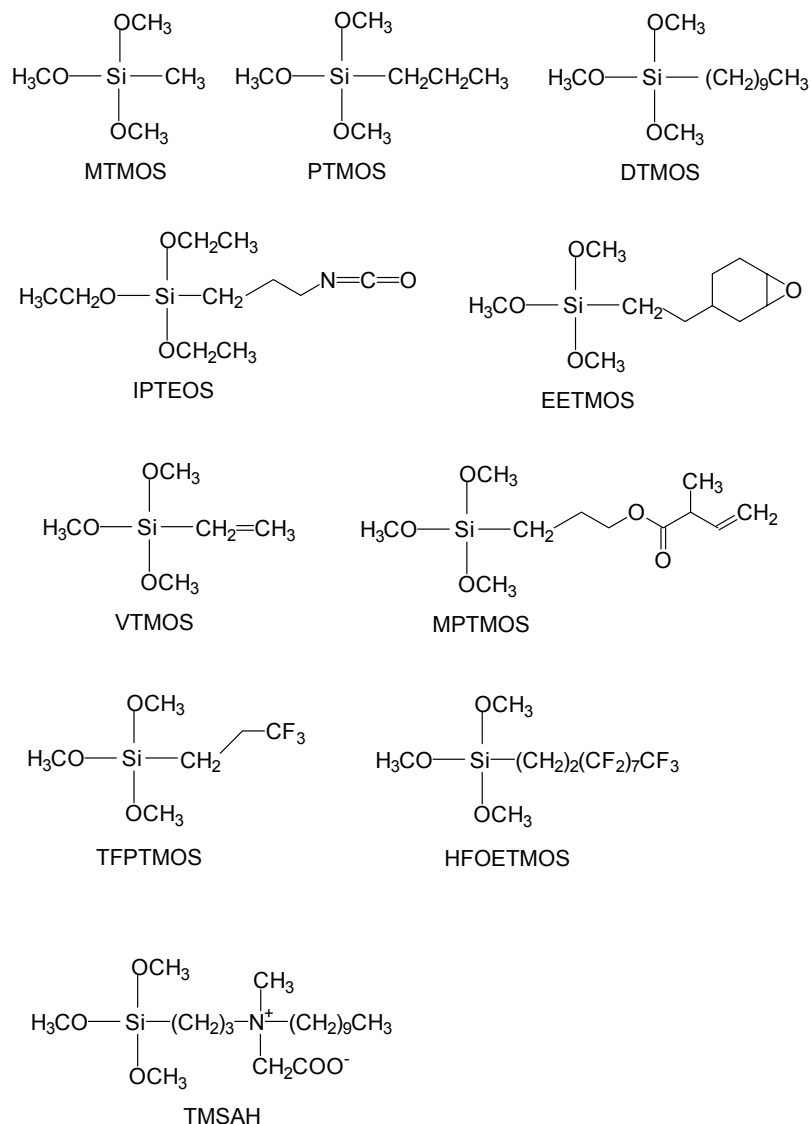


Figure 2: Chemical structure of various organo-silanes applied for wood modification

The decay resistance against basidiomycete attack was enhanced by applying the amphoteric quaternary ammonium compound 3-(trimethoxysilyl)propyl (carboxymethyl) decylmethyl ammonium hydroxide inner salt (TMSAH, Fig. 2) in the sol-gel process. SiO<sub>2</sub>-TMSAH and TMSAH composites were very resistant against brown-rot decay by *Tyromyces palustris* but displayed a low resistance against *Coriolus versicolor* (Tanno *et al.* 1998, Saka *et al.* 1999, 2001). Treatment of hardwoods and softwoods with polymerisable  $\gamma$ -methacryloxypropyl trimethoxysilane (MPTMOS, Fig. 2) decreased the equilibrium moisture content (EMC) and increased the ASE by up to 70%. The change in the wood properties after leaching was relatively low. (Schneider and Brebner 1985, Brebner and Schneider 1985).

Impregnation with propyltrimethoxysilane (PTMOS, Fig. 2) resulted in an ASE of 35 % maximal while EMC was hardly reduced. Decay resistance tests revealed poor activity against basidiomycete fungi for both hardwood (against *Coriolus versicolor*) and softwood species (against *Coniophora puteana*; Goethals and Stevens 1994). Several treatments used two stage impregnation of the sol-gel chemicals. In the first step, the wood is treated with an organo silane which is able to react with the cell wall polymers. Thus, a coupling agent is fixed in the cell wall

which can be linked in a second step by tetraalkoxy metal compounds such as TEOS or tetraisopropyl titanate (TPT). As coupling agent, 3-isocyanatepropyl triethoxysilane (IPTEOS, Fig. 2) was covalently fixed to the cell wall. In a second step, tetraisopropyl titanate was used for cross-linking (Saka and Yakake 1993). The highest ASE of the IPTEOS compounds was about 60% (20% WPG). However, additional treatment with TPT further increased the ASE up to 80% (70% WPG) while specimens which were treated with TPT alone showed negative ASEs.

A similar approach combined organo-functional silanes with TEOS treatment (Ogiso and Saka 1994). IPTEOS,  $\beta$ -(3,4-epoxycyclohexyl) ethyl trimethoxysilane (EETMOS), vinyl trimethoxysilane (VTMOS) and  $\gamma$ -methacryloxypropyl trimethoxysilane (MPTMOS) were used to fix silanes to the cell wall (VTMOS and MPTMOS were polymerised by initiation with benzoyl peroxide). The ASEs of IPTEOS and EETMOS composites were between 30-40% (after first impregnation) and increased linearly up to about 55% after TEOS treatment. In the VTMOS composites, the ASE increased linearly with the WPG to about 40% and was partly increased after TEOS treatment. However, cross-linking of the silicon-functional sites apparently did not occur. For the MPTMOS-SiO<sub>2</sub> composites, ASEs up to 60% were achieved.

### **Micro-emulsion technology**

Coatings and primers based on the micro-emulsion technology have been developed for surface treatment of wood and masonry. The system consists of different silicon polymers in form of so called micro-emulsion in water with a particle size from 10 to 80  $\mu\text{m}$  (Gerhardinger *et al.* 1996, Hager 1995). In comparison to "macro"-emulsions of an oil phase in water, which require an emulsifier, the micro-emulsion technology applies an additional co-emulsifier that interferes with the quasi-crystalline monomolecular surfactant film. The micro-emulsion typically consists of an agent to be emulsified (silane, siloxane or polysiloxane), an emulsifier (silane, siloxane) and a co-emulsifier (functional polysiloxane). Both emulsifier and co-emulsifier in the micro-emulsion technology are active ingredients at the same time and lose their ability to emulsify after drying. When poured into water the micro-emulsions are activated since hydrolysis and condensation occurs. Therefore, dilution should take place directly before the application due to a growing particle size. The application of SMK micro-emulsions on wood caused high water repellence (reduction of water uptake up to 70% after two years of natural exposure) and prevented micro-cracks (fibre separation) due to weathering (Hager 1995, Lukowsky *et al.* 1997). The dimensional stability was not improved (Lukowsky *et al.* 1997).

### **Chlorosilanes and trimethylsilyl derivatives**

The decay resistance of chlorosilane treated wood was tested against *Coriolus versicolor* (white-rot) and five brown-rotters (Owens *et al.* 1980). All treated samples showed significantly lower weight loss than untreated controls. Tetrachlorosilane (SiCl<sub>4</sub>), methyltrichloro silane (CH<sub>3</sub>SiCl<sub>3</sub>), dimethyldichloro silane ((CH<sub>3</sub>)<sub>2</sub>SiCl<sub>2</sub>), methyldichlorohydrogen silane (CH<sub>3</sub>SiHCl<sub>2</sub>) and trimethylsilyl chloride (CH<sub>3</sub>)<sub>3</sub>SiCl were tested, applying basic hydrochloric acid acceptors (triethylamine, formamide, dimethylformamide) as well as hexane as solvent (Stevens 1981, 1985). The decay resistance of wood treated with SiCl<sub>4</sub>, (CH<sub>3</sub>)<sub>3</sub>SiCl and CH<sub>3</sub>SiCl<sub>3</sub> was very low, while CH<sub>3</sub>SiHCl<sub>2</sub> and (CH<sub>3</sub>)<sub>2</sub>SiCl<sub>2</sub> caused a considerable reduction of weight loss (5-10% compared to 25-34% in the controls). The efficacy of chlorosilanes against blue stain fungi and moulds was low. Beech wood meal and beech beads as well as small pieces of white fir were silylated with trimethylsilyl chloride (Zollfrank 2001), 1-(trimethylsilyl)-imidazole and N-(trimethylsilyl)-acetamide (Zollfrank and Wegener 2002). Further transmission electron micro-graphs showed that silylation mainly took part on the lumen-faced side of the cell wall and that half of the S2 wall appeared to be silylated (Zollfrank 2001, Zollfrank and Wegener 2002). Maritime pine sapwood was esterified with compounds bearing trimethylsilyl groups: 3-trimethylsilylpropanoic anhydride (I), 2-trimethylsilylmethylglutaric anhydride (II), trimethyl-

silylketone (III, Sèbe and De Jéso 2000). ASE of specimens treated with I and II increased with WPG and amounted to about 75% and 70%, respectively. These values were stable after three leaching cycles. Dimensional stability of wood treated with III (ASE 59% at WPG of 22%) decreased significantly after 5 leaching cycles (32%).

#### ***Surface modification and hexamethyldisiloxane-plasma coating***

A three-step treatment based on a chemical fixation was reported for surface treatment: (1) esterification with maleic anhydride, (2) etherification with allyl glycidyl ether and (3) hydrosilylation with hydride-terminated silicones (Sèbe and Brook 2001). The silylated wood showed excellent hydrophobicity: the contact angles of water were higher than both untreated and oligoesterified wood (after two modification steps) and initially amounted to about 140-150° (Sèbe and Brook 2001).

Surface modification with cold plasma is a dry process, which alters only the outermost layer of the surface (Denes *et al.* 1999). Wood plasma coating with hexamethyldisiloxane (HMDSO) displayed a water contact angle higher than 120° and water uptake in an immersion test was significantly reduced (Cho and Sjöblom 1990, Denes *et al.* 1999). HMDSO treatment did not result in an improvement in the adhesion of polypropylene film to wood (Mahlberg *et al.* 1998).

## **CONCLUSIONS**

Several studies on the application of silicon compounds for wood modification have been reported which describe the utilisation of a wide variety of different chemicals. Some of the treatments reported address more academic and fundamental questions *e.g.* related to the controlled alterations in specific wood properties (Sèbe and De Jéso 2000, Zollfrank 2001, Zollfrank and Wegener 2002). Various wood properties such as dimensional stabilisation, moisture uptake, weathering and fire resistance, as well as durability can be improved. However, some of the modifications impart certain drawbacks to the wood. Thus, although water glass brought about a good decay resistance, its alkaline nature partly tended to destroy the polymeric structure of wood due to hydrolysis. As a consequence, strength properties were reduced and browning occurred especially when treated wood was dried at high temperature.

Other treatments are able to improve various wood properties without negative impacts on others but the treatment procedures appear to be too complicated to be feasible in practice. This is especially true for those modifications that are performed in several steps or require expensive organic solvents and a costly curing procedure after each step of the treatment. As an example the additional precipitation of silicates in water glass treated wood by infiltration of salts are to be named (Furuno *et al.* 1991, 1992). Two-stage modification processes with organo-silanes in the first step followed by applying sol-gel chemistry in a second step are additional examples (Saka and Yakake 1993, Ogiso and Saka 1994).

A careful evaluation of the durability reported for the various treatments let us consider that in many cases the decay resistance was improved insufficiently when silicon compounds were applied alone. For this reason, silicon treatment was combined with fungicides such as boron, quaternary ammonium compounds or chitosan (Tanno *et al.* 1998, Yamaguchi 2001, Inoue and Tsujimura 1996). Inorganic gels which derived from the sol-gel process were proposed to function as controlled release matrix for fungicides (Böttcher *et al.* 1999).

A comparable tendency could be observed related to fire resistance: although some silicon systems alone have been reported to improve the fire resistance the combination with other compounds was much more successful *e.g.* combination of water glass with boron compounds

(Furuno *et al.* 1991, 1992, 1993) or incorporation of  $P_2O_5$ ,  $B_2O_3$  or  $Na_2O$  into  $SiO_2$ -gel systems (Miyafuji and Saka 1996, Saka and Tanno 1996, Saka *et al.* 1998, Saka *et al.* 2001, Miyafuji and Saka 2001, Li *et al.* 2000, 2001).

Several formulations which contain organo-silicon monomers or polymers are able to cause excellent water repellence without significantly reducing the dimensional stability and the moisture uptake of wood (micro-emulsion technology, polyalkylsiloxanes; Hager 1995, Belyi *et al.* 1985). Because of their high chemical and weathering stability the application of these formulations on wood exposed to conditions belonging to hazard class III (EN 335, outside exposure without soil contact) is recommended.

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**(NEW) CHEMICALS**  
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## Wood Modification by Sol-Gel Derived Precursors

Buecker, M., Boecker, W., Reinsch, S., Unger, B.

Federal Institute for Materials Research and Testing (BAM), Berlin, Germany, michael.buecker@bam.de

**Keywords:** silica-sol treatment, wood-inorganic composite, water repellency, environmental stability

### ABSTRACT

Wood as a renewable primary product offers a lot of useful properties, *e.g.* good specific mechanical properties, pleasing appearance, easy machining. Some disadvantages, such as deficient dimensional stability resulting from interaction with water (swelling, shrinkage), low resistance against attacks of fungi and insects, and low resistance against fire, often require an additional treatment to protect the wood. In this study, modified wood composite materials using SiO<sub>2</sub> as modifier component are presented. Low cost indigenous wood species (pine, beech) were infiltrated with sol-gel derived liquid precursors which can be transformed into solid glass-like substances after heat treatment at moderate temperatures. This procedure results in organic (wood) - inorganic (silica phase) composites with reduced dimensional changes caused by blocking most of the OH-groups of the wood constituents at the exterior and interior surfaces. Additionally, the resistance against biological deterioration is improved. Because of the absence of health threatening substances, disposal as potential hazardous waste is no longer required. The presented work reports on the processing of the wood-inorganic composites and their water repellency and environmental stability properties.

### INTRODUCTION

Many existing processes for enhancing wood properties have led to partial successes only. In some instances, the improvement of durability even results in reduction of the mechanical strength. This is the case *e.g.* for modification of wood by heat treatments (Viitanen *et al.* 1994). The typical method of wood modification is a preservative treatment with a biocide, some of these processes may result in a negative environmental impact. In many cases, impregnated timber has to be disposed of as potential hazardous waste, *e.g.* after treatment with Cu or Cr containing compounds, or with certain organic substances. The aim of this study is the development of environmentally benign modified wood composite materials on the basis of low cost indigenous wood species (pine, beech) and SiO<sub>2</sub> as the modifier component. The cell walls of wood consist mainly of cellulose, lignin and hemicellulose. The reactive hydroxyl groups of these molecules are responsible for many physical and chemical properties of the wood. In this study, a sol-gel process was applied to prepare tetraethoxysilane (TEOS) derived precursors. Treating of wood with these precursors should result in a reaction with the hydroxyl groups of the wood and lead, after a moderate thermal treatment, to the formation of a wood-inorganic composite. The modified wood shows enhanced properties, like enhanced dimensional stability, without loss of mechanical strength and an improved resistance against biological deterioration. Some approaches are known from literature (*e.g.* Saka 1992 and 2001, Ogiso 1994, Miyafuji 1999, Boettcher 2000, Scheithauer 1998).



## EXPERIMENTAL

### ***Wood specimens***

Standard samples of (50 x 25 x 15) mm<sup>3</sup> of pine sapwood (*Pinus sylvestris* L.), were used for most of the tests. The 4-point-bending test was performed with samples of (360 x 20 x 20) mm<sup>3</sup> according to DIN standards (DIN 52186, 1978). All samples were oven dried before treatment for obtaining a defined reference of weight and volume.

### ***Impregnation liquids***

The silica sols were prepared from tetraethoxysilane (TEOS) in a solution of ethanol, by means of acid-catalysed hydrolysis and condensation. The degree of cross-linking of the precursors is controlled by concentration of constituents and synthesis procedure.

### ***Preparation of wood-inorganic composites***

The samples were treated with the sol-gel derived liquid precursors, or resin, according to DIN/EN (DIN/EN 113, 1996). The oven-dried samples were impregnated under vacuum, stored for one day under normal pressure and 20 °C and finally, heat treated at 103 °C for drying of the TEOS derived gel. By measuring the weight of the composite specimens after this heat treatment, the weight percent gain (WPG) was determined on the basis of the oven dry weight of the untreated sample. The distribution of the TEOS derived gel in the wood was determined by means of electron probe microanalysis (EPMA).

### ***Test of water repellency***

To evaluate the moisture-repellent property of the composites, the samples were stored in 100% relative humidity at 20 °C and atmospheric pressure for about 12 weeks. All samples were oven dried to get a starting point of 0 % wood moisture content. The changes in the weights of the samples due to moisture absorption were measured every day, at first and later, every week. Additionally, the samples were placed in distilled water at 20 C. The changes in weight, due to water absorption, were measured every day.

### ***Test of natural durability***

The wood inorganic composites were tested for their resistance against biodeterioration by fungi. The tests were performed according to DIN standards: The method of test for determining the protective effectiveness against wood destroying basidiomycetes was according to DIN/EN 113 (1996). The resistance against active timber infestation was tested with the most common pest of timber in middle Europe according to DIN: "Determination of the preservative action against recently hatched larvae of *Hylotrupes bajulus*" and "Determination of the toxic values against larvae of *Hylotrupes bajulus*", respectively (DIN/EN 46 and DIN EN 47, both 1990).

## RESULTS AND DISCUSSION

A comparison of conventional wood preservative treatment and the developed treatment used in this study is shown in Figure 1. Both methods use similar processing steps. The advantage of the silica sol treatment is a simple disposal of the used timber without environmental impact. After usage, the wood contains no hazardous substances making dumping or combustion possible.

The method of synthesis is the most critical parameter for the morphology of TEOS derived gels and therewith the chemical bonding to the wood cell walls. Thus, weight percent gains (WPG) between 5 and 50 % were realised in this study. In the literature, WPG's up to 35 % were reported after a similar treatment with liquids based on TEOS (Ogiso 1994), but in these cases the dimensions of samples were noticeably smaller (sample thickness of 1 – 2 mm), than in this study. Some properties of the wood-inorganic composites are presented next.

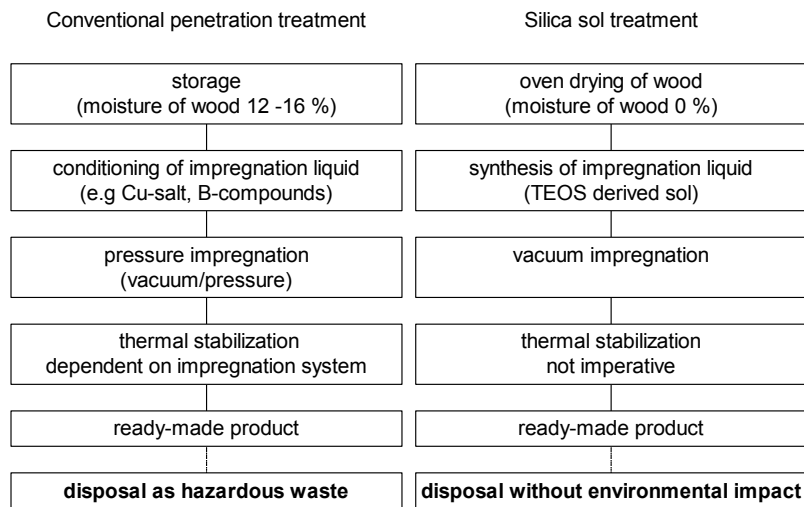


Figure 1: Comparison of treatment processes, left: conventional impregnation, right: "silica-sol-process".

### Water repellency

Figure 2 shows the increasing moisture content as a function of time of untreated wood and wood-inorganic composites with different processing parameters of the precursors (Sol2, 3 and 4). The increasing Sol –Number shows the enhancement of the precursors by a variation of the composition (TEOS:Ethanol:H<sub>2</sub>O:Acid) in the course of the presented research project. The samples were stored in relative humidity of nearly 100 %, atmospheric pressure and 20°C.

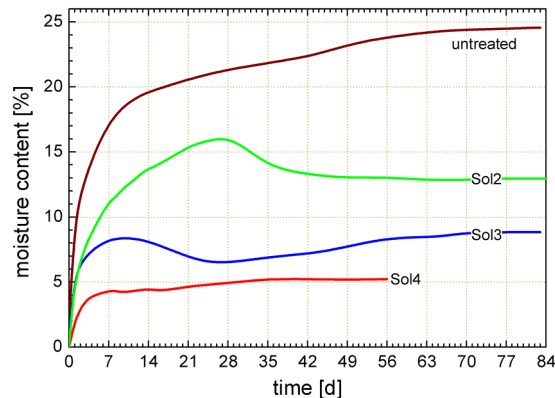


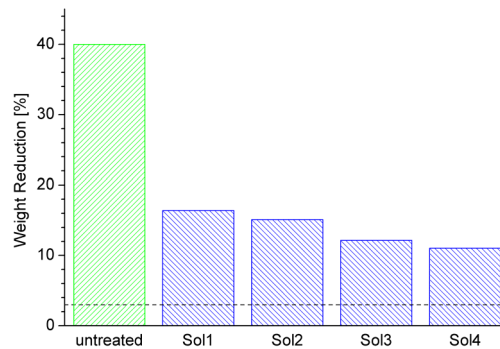
Figure 2: Time dependent moisture content (weight percent) of pine wood samples in relation to different Sol treatments (Sol2 to 4). The samples were stored on a relative humidity of nearly 100 %, atmospheric pressure, and 20 °C.

For these storage conditions, the untreated pine-wood (0 % humidity) reached fiber saturation moisture (26 - 28 %) (Lohmann 1990) after a few days. In comparison, the moisture content of wood-inorganic composites reached much lower values. The silica sol was enhanced by adapting the chemistry to the needs of the wood during the last two years of research. For the latest Sol (Sol4) the moisture content was about 5% after an exposure of 8 weeks. Likewise, the anti-shrinkage-efficiency was substantially improved by the silica sol treatment. For high WPG's, the swelling of the samples was reduced up to 60 %. Furthermore, samples were submerged in distilled water for 26 days (Buecker *et al.*, 2001). The water absorption of wood-inorganic composites ( $\approx 50$  % WPG) was about 75 % of weight gains of untreated wood at the end of this

test. Additionally, the rate of water absorption was substantially reduced for the composites. After an exposure of 1 day, the moisture content of untreated wood was 75 % and only 20 % in the case of treated wood.

### ***Environmental stability***

Figure 4 shows the results of biodeterioration tests by fungi. The preservative treatment with TEOS derived gel resulted in a substantial decrease of weight reduction caused by attack of fungi. The precursors (Sol1 to Sol4) are different in their composition and their processing parameters. They have been optimised during the course of the research project. In the best case, the protection led to a weight reduction of only about 12% of the composite. In comparison, with the untreated wood, the attack by fungi was also time-delayed. But still the total weight loss by biodeterioration was higher than the tolerable limit (3%, dashed line in Figure 4) of weight loss according to DIN EN 113. Because biodeterioration by fungi is related to the moisture content of the wood, further development to improve water-repellency should result in an enhanced resistance against fungi. Additionally, some chemical agents with biocidal activity can be incorporated in the silica gel network for better results. In this case, the agent should resist leaching. Therefore environmental impact by the agent is eliminated.



**Figure 3:** Weight reduction by the fungus “*Poria placenta*” after exposure of 16 weeks according to DIN EN 113 of differently treated and untreated pine sapwood samples. The dashed line represents the required limit of weight reduction for no biodeterioration by fungi.

A test of the resistance against active timber infestation was made with larvae of “*Xylophaga*” according to DIN EN 46. The test was performed with 10 larvae in each case on 10 samples and one repetition. In all cases, the larvae failed to attack the impregnated wood. A second test was performed where the larvae are placed into the samples according to DIN EN 47. None of the appointed larvae were able to develop and died off. 76% of the larvae appointed to the untreated control samples were found alive.

## **CONCLUSIONS**

Environmentally benign modified wood composite materials using SiO<sub>2</sub> as the modifier component have been developed. Low cost indigenous wood species (pine) were infiltrated with sol-gel derived liquid precursors, which were transformed into solid glass-like substances after heat treatment at moderate temperatures. This process results in wood-inorganic composites with reduced dimensional changes caused by blocking most of the OH-groups of the wood constituents at the exterior and interior surfaces. Additionally, the resistance against biological deterioration has been improved. In comparison to other treatments, the mechanical properties of the timber have not been negatively affected. Because of the absence of health threatening substances disposal as potentially hazardous waste is not required. Further investigations of

organic modifications of the TEOS derived sol have been started to achieve reduced brittleness of the gel-phase. Supplementary examination of the heat treatment of the impregnated wood should lead to a stable bonding of the gel-phase in the composite.

### ACKNOWLEDGEMENT

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## Use of di-Carbamate Based Resins for Wood Preservation.

Gilles Chaumat, Christophe Albino, Jean Philippe Bertrand and Marie Angélique Languille.

ARC-Nucléart, CEA-Grenoble, 17 rue des Martyrs, 38054 Grenoble Cedex 9, France

**Keywords:** wood modification, impregnation, carbamate.

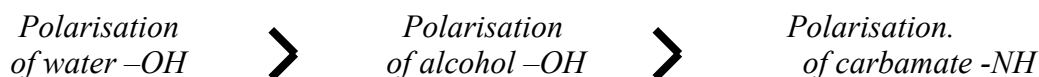
### ABSTRACT

Wood is less used for outdoor applications nowadays, mostly due to the fact that the common fast-growing European species have little natural resistance to bacteria, moisture, thermal ageing and U.V. radiation. Wood used outdoors consists of either exotic species imported from developing countries or timber treated by permeation with very toxic chemicals (CCA). But these practices are becoming increasingly limited and are certain to disappear in the short term. This paper deals with the use of di-carbamate chemicals for improving wood stabilisation. These resins are products obtained from chemical reactions between a di-isocyanate such as Hexamethylene Di-Isocyanate (HDI), or Toluene Di-Isocyanate (TDI) with a mono-alcohol such as ethanol. For both di-isocyanates considered, we obtained a di-carbamate in a solid state at room temperature up to 80°C that is fully hydrophobic, but very soluble in alcohol. It appears that these molecules are able to diffuse into the cell walls and keep them swollen, even after a drying phase. Hydrogen bonds established between carbamate functions and hydroxyl groups of ligno-cellulosic materials could probably explain this phenomenon. After one year of work performed in our laboratory, it is now possible to propose an optimised treatment of wood using di-carbamate impregnation. Interesting results have been obtained in terms of the stability of the wood during the drying/wetting cycle: ASE of 60-70% are easily reached by this process. Furthermore, the hydrophobic nature of the di-carbamate ensures that the resin is well fixed inside the wood cell walls; there is indeed little di-carbamate leaching by water. Nevertheless, this simple permeation treatment remains fully reversible, because it is possible to remove the resin from the wood by using an ethanol solution.

### INTRODUCTION

Wood is less used for outdoor applications nowadays, mostly due to the fact that the common fast-growing European species have little natural resistance to bacteria, moisture, thermal ageing and U.V. radiation. Wood used outdoors consists of either exotic species imported from developing countries or timber treated by permeation with very toxic chemicals (CCA). But these practices are becoming increasingly limited and are certain to disappear in the short term. To solve wood conservation problems, several approaches have been investigated. One of them consists in grafting hydrophobic molecules onto the hydroxyl groups of wood: lignin, cellulose and above all hemicellulose. The main common reactive products used for chemically grafting the wood are either isocyanate, epoxide or anhydride reagents (Rowell *et al.* 1994, Hill *et al.* 2000, Militz *et al.* 1993, Ellis *et al.* 1993) Such chemical wood stabilisation is feasible and has been well-known for several decades, but no industrial processes are available because the toxic catalysts and reagents have to be completely cleaned from the wood afterwards, before it can be used. Such post-treatment, which involves cleaning the wood several times in solutions of powerful solvents followed by drying, is not compatible with costs on the wood treatment market.

Another possibility for stabilising the wood involves replacing covalent bonds by "hydrogen bonds". The energy of a hydrogen bond is lower than that of a covalent bond, but it is of the same order of magnitude as the energy between water and wooden hydroxile functions. Indeed, the link between bound water and ligno-cellulosic materials is also a hydrogen bond. This leads to deformation of the wood during drying or wetting phases. Unfortunately, the main known agents of hydrogen bonding are alcohols: polyethylene glycol, glycerol, etc. All these chemicals are water-soluble, and consequently wood treated with these alcohol agents will easily be leached by rainwater. Because of these considerations, our laboratory decided two years ago to assess urethane or carbamate-based chemicals for establishing hydrogen bonds with wood. Indeed, the carbamate function is potentially very interesting due to the polarisation of the N-H function, which is far from that of water but close to that of alcohol:



The main consequence of this feature is that carbamates can be hydrobobic products and therefore not water-soluble, whereas carbamates remain fully soluble in alcohol such as ethanol.

### DETERMINATION OF EXPERIMENTAL CONDITIONS FOR WOOD TREATMENT BY A LINKAGE REAGENT

An important condition for ensuring the efficiency of the treatment is that the carbamate must be well distributed into the cell walls in order to obtain the maximum number of hydrogen bonds between it and the wooden components. This means:

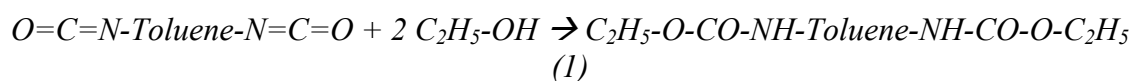
- using short molecules to ensure the good permeation of the wooden structures by the carbamate-base chemicals,
- swelling the wood before introducing the carbamate resins in order to open up the wooden structure. Water may be used as swelling agent.

In contrast to the complex treatment used for grafting wood, classic impregnation by resin is proposed here, without any chemical reaction. This treatment is simple to carry out and requires only heated tanks that can raise the temperature of the solution to 100°C. The main advantages expected from this process are that the treatment is reversible (possibility of recycling the carbamate resins), the wood's mechanical properties are maintained, its visual appearance is unaffected and post-treatment cleaning is unnecessary.

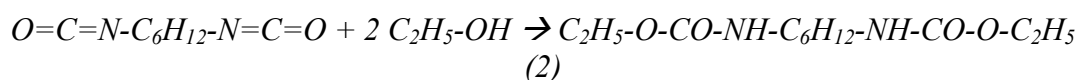
### CHOICE OF CARBAMATE RESINS

Except for some biocides and highly toxic molecules, no short molecules of carbamate are available commercially, so all the resins used for our experimental testing are manufactured by our laboratory. Fortunately, these resins are easy to produce (see reactions 1 and 2). We used available precursors of polyurethane polymers, i.e. di-isocyanates: either Toluene Di-Isocyanate or TDI (aromatic version) and Hexane-Di-Isocyanate or HDI (aliphatic version). Both di-isocyanates react strongly with ethyl alcohol to obtain di-carbamates:

With TDI reagent, the chemical reaction is:



With HDI reagent, the chemical reaction is:



Both di-carbamates are solid at room temperature. In crystallised form, these carbamates appear as a white wax. It is possible to obtain the TDI-based carbamate in a metastable form by quenching the liquid resin in a transparent glass. With both pure carbamates, the melting point is close to 100-120°C. There are thus two ways of using the carbamate resins:

- either performing the permeation treatment of pure carbamate above its melting point,
- or using ethanol as carbamate solvent to work at lower temperatures [60-80°C]

The second solution appears to be more appropriate from the industrial point of view; it is possible to work under 100°C and control the quantity of carbamate introduced into the wood. Indeed, impregnation with pure resin will unnecessarily increase the consumption of carbamate by filling up open pores in the wood; it is only necessary to ensure that the di-carbamate permeates the cell walls themselves.

### OPTIMISATION OF OPERATING CONDITIONS

The technical parameters to be taken into account for improving the efficiency of the treatment are:

- the amount of water in the wood before treatment, to ensure swelling: range [10-50%<sup>(1)</sup>];
- ethyl alcohol as di-carbamate solvent: range [0-80%<sup>(1)</sup>];
- the amount of di-carbamate from HDI resin itself as linkage agent: range [10-50%<sup>(1)</sup>].

The impregnation temperature was maintained constant at 60°C. Permeation was carried out in two stages: 2 hours under vacuum followed by immersion lasting 24 hours in the ethanol + carbamate mixture.

The samples consisted of rectangular wooden pieces measuring 200 x 70 x 4 mm; the longitudinal fibres were oriented parallel to the length of the sample.

To assess the efficiency of the treatment, a "pseudo ASE" calculation was considered, based only on measurement of the width of the sample: longitudinal orientations and the contribution of the 4mm thickness are negligible. Three reproducibility points were taken for each measurement.

The "pseudo ASE" is defined as follows (Eq 3 and Eq 4):

$$\text{Pseudo ASE (\%)} = (S_2 - S_1) \times 100 / S_1 \quad (3)$$

in which  $S_2$  is the swelling coefficient after treatment and  $S_1$  before treatment.

$$S_i (\%) = (L_2 - L_1) \times 100 / L_1 \quad (4)$$

in which  $L_2$  is the width of the wet sample and  $L_1$  that of the dry sample.

To ensure correct exploitation of the results and to cancel any possible effect of resin leaching by water, the ASE was only considered after the fourth wetting/drying cycle.



## RESULTS AND DISCUSSION

The results in terms of ASE are summarised in Table 1 below:

*Table 1: Pseudo ASE versus operating parameters.*

<b>Water content in the wood %<sup>(1)</sup></b>	<b>Carbamate content %<sup>(1)</sup> in the solution</b>	<b>Ethanol content %<sup>(1)</sup> in the solution</b>	<b>Pseudo ASE %</b>
10			21
20			27
30	10	90	34
40			33
50			35
10			50
20			37
30	20	80	51
40			46
50			28
20			60
30	30	70	74
40			62
50			72
20			69
30	40	60	73
40			67
50			75
10			70
20			67
30	50	50	68
40			72
50			67

<sup>(1)</sup>: Weight percentage.

The main sensitive parameter is the percentage of di-carbamate resin: below a threshold of 30%, there is no improvement in ASE, while at 30% or more, ASE levels of 60-70% are easy to reach. The other parameter, the initial water content in the wood before permeation treatment, appears to be less sensitive; the treatment may be performed independently of the initial moisture in the wood. This parameter is potentially interesting from the industrial point of view; it means that it is not necessary to oven-dry a wood before stabilisation treatment. Figure 1 shows an example of ASE curves versus the number of wetting/drying cycles. It can be seen that there is no leaching effect. The pseudo-ASE remains constant higher than 60% ASE.

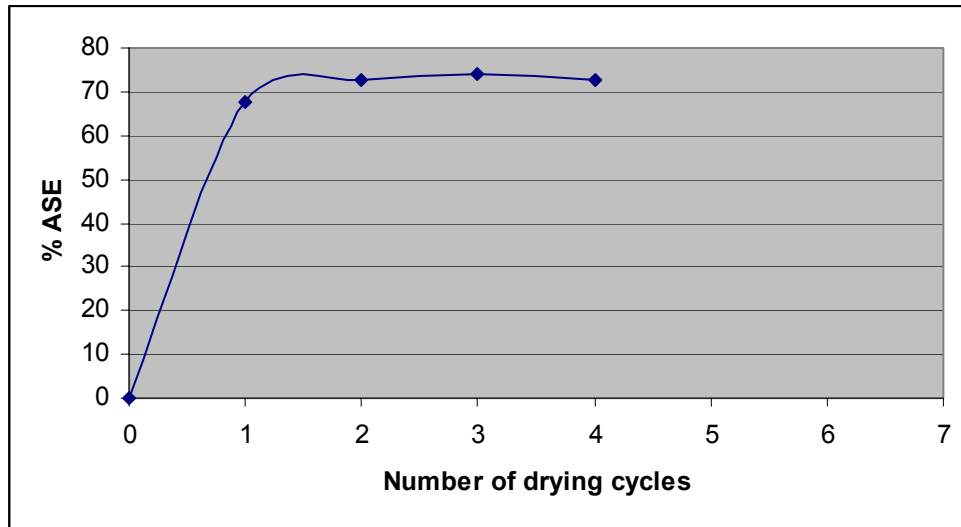


Figure 1: ASE % with 30% water in wood , 40% carbamate, 60% ethanol.

## CONCLUSIONS

This first attempt demonstrates that it is possible and interesting to find organic components that are sufficiently hydrophobic to avoid water leaching and are sufficiently polar to produce good "hydrogen links" with wood hydroxiles to stabilise them: such organic functions can be selected from the urethane or carbamate functions with short molecules, for instance di-carbamates. The wood is partially stabilised by the carbamate resins (ASE >50% after 4 wetting/drying cycles). The easiest permeation method consists in dipping the wood in ethyl-alcohol solution containing at least 30% of carbamate. Further analyses are needed to confirm the advantages of this technique for industrial activities. For instance, we have no complete information concerning:

- resistance to fungi, bacteria and insects
- resistance to ultra-violet radiation
- compatibility with finishing works: varnishing, sticking, pumicing, etc.
- resistance to fire
- the reversibility of the treatment so that the resins can be recovered when the treated wood is at the end of its working life.

Our study will continue investigating some of the items listed above, especially rot resistance. We have noted that boric acid is soluble in a solution of ethanol-carbamate. Consequently, carbamate may be an efficient means for trapping boron in the wood as a biocide.

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## Properties of Wood Treated with Hydrophobisation Agents

Anne-Christine Ritschkoff<sup>1</sup>, Riitta Mahlberg<sup>2</sup>, Leena Suomi-Lindberg<sup>3</sup>, Liisa Viikari<sup>4</sup>, Antti Nurmi<sup>5</sup>

<sup>1</sup>VTT Building and Transport, P.O. Box 1806, 02044 VTT, Finland, anne-christine.ritschkoff@vtt.fi

<sup>2</sup>VTT Building and Transport, P.O. Box 1806, 02044 VTT, Finland, riitta.mahlberg@vtt.fi

<sup>3</sup>VTT Building and Transport, P.O. Box 1806, 02044 VTT, Finland, leena.suomi-lindberg@vtt.fi

<sup>4</sup>VTT Biotechnology, P.O. Box 1500, 02044 VTT, Finland, liisa.viikari@vtt.fi

<sup>5</sup>VTT Building and Transport, P.O. Box 1806, 02044 VTT, Finland, antti.nurmi@vtt.fi

**Keywords:** Wood modification, hydrophobic wood, siloxane treatments

### ABSTRACT

Contact of wood with water causes a number of unfavorable phenomena in the wood structure *e.g.* dimensional changes and susceptibility to fungal growth (mould, blue stain, decay). Access of water to wood can be reduced by treating wood with water repellents. In terms of overall wood protection, the most promising hydrophobisation systems are the ones introducing the hydrophobic agent into close contact with the wood cell wall components. In this work, the applicability of hydrophobic treatments as new generation wood preservatives has been studied by using silicon-based compounds. The compounds were chosen on the basis of their chemical structure and of their predicted reactivity. Chemical analyses as well as physical tests of the treated wood showed that the most promising hydrophobisation agents had come into contact and in some of the cases even bonded with the cell wall components. The results indicate that the siloxane compounds studied have efficacy against wood decaying fungi. Leaching does not affect the efficacy of the treatments, which is also an indication of fixation of the compounds in the wood structure. Some of the compounds studied prevent the growth of mould and blue stain on the treated wood material. As expected, the glueability properties of hydrophobised wood surfaces differ from those of untreated wood. The performance of traditional wood adhesives with the hydrophobised wood was proven to be unsatisfactory. The applicability and performance of different silicon-based hydrophobisation treatments of wood will be further studied in collaboration with several European research institutes and industry within a project funded by the EU.

### INTRODUCTION

Penetration of water into the wood structure can be reduced by treating wood with water repellents. When these chemicals come into contact with the components of wood cell wall and prevent the interaction between water and cellulose in the cell wall, improvement in the dimensional stability of the wood is achieved. In addition, decrease in the moisture content of wood makes wood less susceptible to biological degradation, *i.e.* attack by fungi. Silicon-based water repellents are available for masonry and textile applications. Similar products/agents can be considered feasible for hydrophobicity treatments of wood, as well. Organosilicon compounds possess some properties which make them distinctively attractive for wider use in wood industry. Besides having excellent water repellency properties, these compounds are thermally stable and permeable to water vapour (Hager 1995). Furthermore, silicones are reported to be rather inert to living organisms (Bradley *et al.* 1994, Siddiqui *et al.* 1994). In the present work, the effect of commercially available siloxane emulsions on the dimensional stability, glueability and biological resistance of pine sapwood was studied.

## EXPERIMENTAL METHODS

Two commercially available siloxane products (SilT and SilS) were used for vacuum impregnation treatments of pine (*Pinus sylvestris*) sapwood samples of 20 x 20 x 5 mm (radial x tangential x longitudinal). The treatment products were aqueous emulsions of polydimethylsiloxanes.

The dimensional stability, glueability and biological resistance against mould, blue stain and decay fungi of the treated samples were evaluated by means of laboratory tests. The prevention efficacy of the two siloxane products against the brown-rot fungi *Coniophora puteana* and *Poria placenta* was examined according to the EN 113 standard which was slightly modified, e.g. in terms of sample sizes. The wood samples were leached according to modified EN 84 standard prior to the decay test. The resistance of the treated wood against blue stain and mould were carried out in incubator chambers according to a VTT-method. The degree of growth was estimated according to the VTT growth index (see Fig. 3). For testing the bondability of the treated wood, such traditional wood adhesives as resorcinol formaldehyde (RF), emulsified polymer-isocyanate (EPI) and polyvinyl acetate (PVAc) were used. The tests were carried out according to the EN205 standard (lap joints). The test samples were conditioned 7 days at standard atmosphere (20 °C and 65 % relative humidity) prior to the shear strength testing.

## RESULTS AND DISCUSSION

The siloxane treatments studied slightly improved the dimensional stability of pine sapwood compared to the untreated references (Table 1). Indirect evidence on the contact/interaction of the siloxanes with the cell wall components is obtained if increase in the dry volume of the samples is observed after the treatments. This bulking effect was more pronounced in the case of the siloxane treatment SilS, whereas the changes in the dry volume of the samples due to SilT treatment was almost negligible (Table 1). The bulking effect partially explains the differences in the effect of the two treatments on the dimensional stability of wood.

**Table 1: Effect of the siloxane treatments on the dimensional stability and on the change in the dry volume of the pine sapwood samples.**

Treatment	Treatment level <sup>a</sup>	Dimensional stability (ASE) <sup>b</sup>	Increase in dry volume due to treatment
	[%]	[%]	[%]
Untreated	-	-	-
SilS	16	8.4	1.2
	28	12.6	2.0
SilT	15	≈ 0	0.3
	30	6.0	0.4

<sup>a</sup> weight gain

<sup>b</sup> antishrink efficacy: the higher the ASE, the better dimensional stability compared to untreated wood (Rowell 1984)

The biological tests clearly indicated that the siloxanes studied have efficacy against wood decaying fungi. Leaching does not affect the efficacy of the treatments which is an indication of fixation of the compounds in the wood structure (Fig. 1a and b). In addition, the siloxane SilS prevented the growth of mould fungi and blue stain on the treated wood material at high treatment levels (Fig. 2a and b).

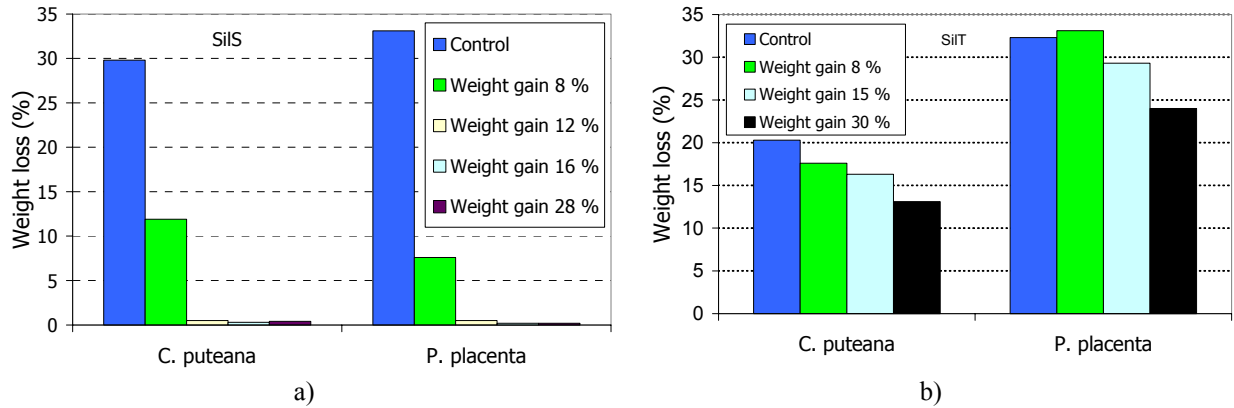


Figure 1: The prevention efficacy of siloxane products against brown-rot fungi *Coriolus puteana* and *Poria placenta*. The tests were carried out with leached samples. The labels indicate the dry weight gains of the samples due to the treatments.

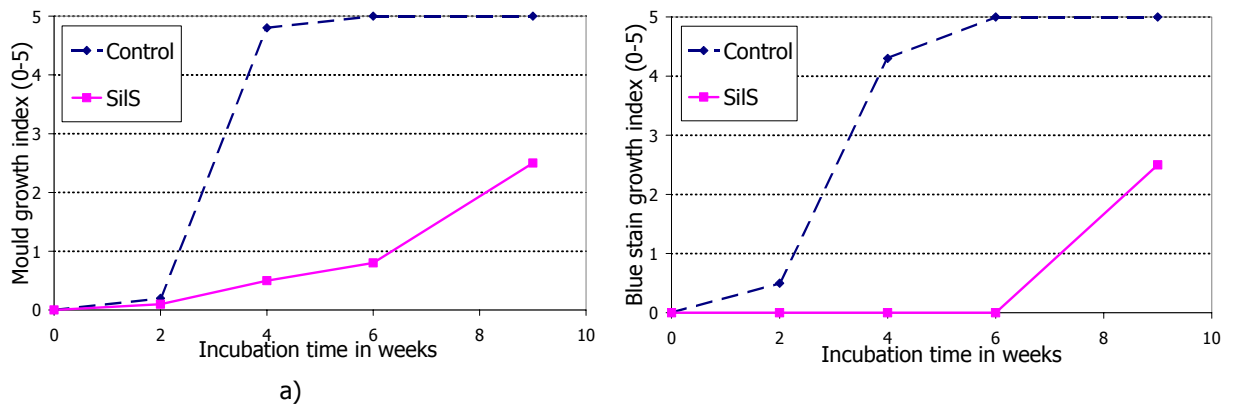


Figure 2: The prevention efficacy of the siloxane treatment SiS against the growth of a) mould and b) blue stain fungi. The treatment level of the samples was 28 % (weight gained). The growth index is evaluated as follows: 0 = no stain/mould present on surface (microscope) 3 = 10-30 % coverage of stain/mould on surface (visual) 1 = small amount of stain/mould on surface (micr.) 4 = 30-70 % coverage of stain/mould on surface (visual) 2 = <10 % coverage of stain/mould on surface (micr.) 5 = > 70 % coverage of stain/mould on surface (visual).

The gluing test showed that adhesion of all the three adhesives to the treated wood surfaces compared to the control samples was inferior (Fig. 3). However, some of the RF-glued test samples gave shear strength values equal to these of control samples, whereas some of the RF-glued samples showed quite unsatisfactory bonding strength. This variability in the test results could not be explained within the project. The glue line formation, especially the penetration of the glues, was examined with a light microscope. For successful gluing, sufficient penetration of the glue into the wood structure is essential. This was not the case with the treated wood specimens (Fig. 4).

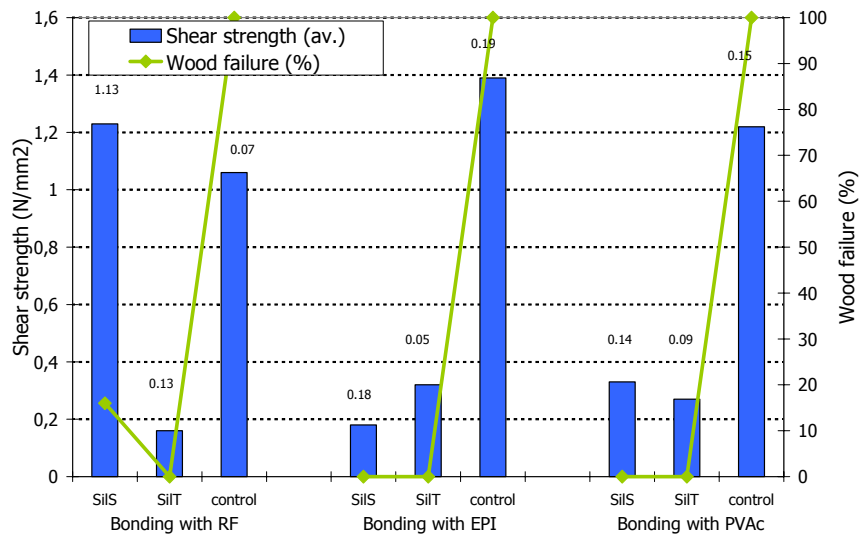


Figure 3: Shear strength and wood failure values of test samples bonded with RF, EPI and PVAc adhesives. Figures on top of the bars indicate the standard deviation for the shear strength values.

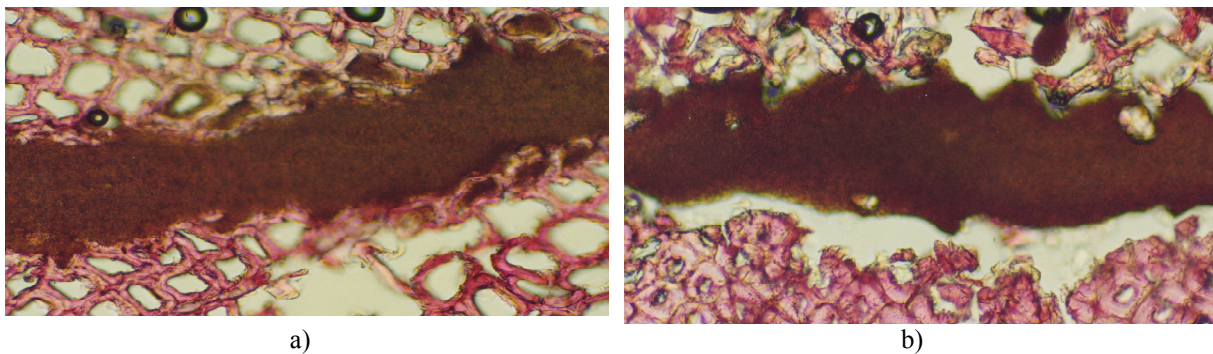


Figure 4: Micrographs of the EPI glue line in a) an untreated test sample and b) a SiIS-treated sample.

## CONCLUSIONS

- Vacuum impregnation of pine sapwood with the siloxanes tested improves the biological resistance and also slightly enhances the dimensional stability of the wood.
- The prevention efficacy of the model siloxanes against decay fungi and the effect of these compounds on the dimensional stability and moisture properties of wood is related to the accessibility of the compound with the cell wall components of wood.
- Bonding of the siloxane-treated surfaces is one of the practical issues necessary to be solved.
- Systematic work is needed in order to find suitable application methods and process parameters for different wood dimensions and species.
- The preliminary results showed the potential of hydrophobisation treatments as moisture and biological damage control agents for wood and this topic will be further studied in collaboration with several European research institutes and industry within a project funded by EU.
- The long-term durability and overall performance of hydrophobised wood in practice are still unknown. These issues will also be focused on in the future.

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## Short-duration Impregnation of Wood with Melamine Resins

I. Rosca<sup>1</sup>, I. Gsoels<sup>1</sup>, M. Rätzsch<sup>1</sup>, H. Schmidt<sup>2</sup>

<sup>1</sup> Kompetenzzentrum Holz GmbH (Wood K plus), St.-Peter-Str. 25, Linz, Austria

<sup>2</sup> Johannes Kepler University, Institute of Chemical Technology of Organic Materials, Altenberger Str. 69, Linz, Austria

**Keywords:** wood-impregnation, dimensional stability, compression tests, moisture sorption.

### ABSTRACT

Untreated and ammonia treated spruce wood were impregnated with modified melamine resins with the aim of investigating the impregnation duration and depth in case of the two different wood states and its effect on various characteristic parameters of the final impregnated wood samples. The resin-impregnated wood samples were air-dried and then oven-dried in order to permit the cross linkage of resins. The experiments showed that the ammonia pre-treatment allowed shortening of the duration of impregnation from approximately 24 hours to 2-6 hours. Dimensional stability, mechanical properties and water repellence of impregnated wood samples were tested. Ammonia pre-treatment of wood allows a better penetration of melamine resins into the cell wall that can be expressed by higher compression strengths of the ammonia-resin impregnated samples compared to untreated wood samples impregnated with the same resins.

### INTRODUCTION

Many properties of solid wood are often perceived as negative by the end-user, such as dimensional instability with changing moisture content, low natural durability of many species, photo yellowing or unsuitable mechanical properties. A promising way to improve wood properties is through controlled chemical modification. The real challenge for chemists is to develop processes that yield the desired products and also are efficient and environmentally friendly. In the last decade, the interest in the manufacture of wood polymer composites (WPC) has been increased because of the need to find viable alternative uses for waste plant fibre material and thermoplastics. The interest in WPC production is also based on the improvements of solid wood/or wood fibres / properties through the impregnation with various monomers and thermosets. Melamine-formaldehyde and melamine urea-formaldehyde resins are commonly used thermosetting wood adhesives. Both resins give good moisture resistance and adhesive performance and tend to have lower formaldehyde emission compared to urea-formaldehyde resins (Pizzi *et al.* 1996). Ammonia has a high affinity to all three main wood components, cellulose, hemicellulose and lignin: resulting in a range of physical and chemical transformations of the wood (Schuerch 1963, 1964). Ammonia is able to penetrate into the crystalline regions of the cellulose and leads to a temporary transformation of Cellulose I into Cellulose III, the lignin-carbohydrate complex is disrupted. The ammonia treatment does not change significantly the content of cellulose, hemicellulose and lignin in the substrate, but the swelling effect is important and the pore structure is modified. After the evaporation of ammonia, the wood returns to its solid state, even to a more compacted structure (Berzins and Rocens 1970). Based on the physical and mechanical changes caused by an ammonia treatment of wood, it can be presumed, that as long the ammonia is not evaporated, the penetrability of chemical substances can be improved. This work is focused on the possibility to improve the impregnation of wood with melamine resins through ammonia pretreatment and on the evaluation of the properties of obtained WPC.

## EXPERIMENTAL METHODS

### *Wood samples*

Spruce wood boards, conditioned for 6 days at 65% humidity, were selected for this study and cross-sectional wood pieces, 20x20x20mm in size, were cut from these boards. Their dimensions were measured in the tangential (T), radial (R) and longitudinal (L) directions with a precision of 0,01mm with a screw micrometer. The weight of samples was also measured with a precision of 0,1mg. After the resin impregnation of ammonia pre-treated samples, the dimensions of the wood specimens were measured again and the relative swelling (SE, %) and the weight percent gain (WPG, %) were calculated.

### *Melamine resins*

Two MF resins were chosen:

- Resin A, an experimental product from Agrolinz Melamin, is a fully methylated MF resin, with high NH content and a content of solids between 40 and 50%.
- Hilamin PA 43 from Dynea Austria is a partially methylated MFR with high NH content used as 72% solution in water

### *Wood pre-treatment and impregnation*

The ammonia wood pre-treatment was carried out with anhydrous liquid ammonia in a 100 ml reactor at room temperature, at a pressure of 12 bar and duration of 4 hours. The impregnation of wood with resins was performed under vacuum by fully immersing the wood samples in the resin. Samples were periodically taken out from the impregnation solution in order to determine the extent of impregnation from the difference of weights of the impregnated samples and the reference-untreated samples. After the fully impregnation, the wood samples were removed from the resin, blotted dry with tissue paper and cured in an oven successively at 103°C for 3 hours and successively 150°C for 1 hour.

Equations (1) and (2) were used to determine the swelling percent and the weight gain:

$$SE = \frac{V_t - V_0}{V_0} * 100 \quad (\text{for the volumetric swelling coefficient}) \quad (1)$$

$$WPG = \frac{W_t - W_0}{W_0} * 100 \quad (\text{for the weight percent gain}) \quad (2)$$

where  $V_0$  is the sample volume before treatment and  $V_t$  is the sample volume after treatment,  $W_0$  is the sample weight before treatment;  $W_t$  is the sample weight after treatment.

### *Compression strength of composites*

The impregnated and cured spruce wood pieces were tested in compression parallel-to-grain using a Universal testing machine Shimadzu AG-50kNE and following the DIN 52185 method. The compression parallel-to-grain test is suitable for samples with inaccurate orientation of the natural axes and for inhomogeneous samples as long as the adjustment of the grain is accurately parallel. At least 7 samples were measured and from these an average was computed.

### *Water uptake capacity of the untreated and ammonia-treated and resin-impregnated wood samples*

The water uptake capacity was determined as the volume increase of the untreated wood samples and treated wood by immersing them into distilled water for 24 hours, through the swelling coefficient (SE) Eq.(3). The dimensional stability of impregnated wood samples (ammonia pre-treated and untreated) was evaluated as antishrink efficiency (ASE) – Equation (4):

$$SE = \frac{V_2 - V_1}{V_1} * 100 \quad (3)$$

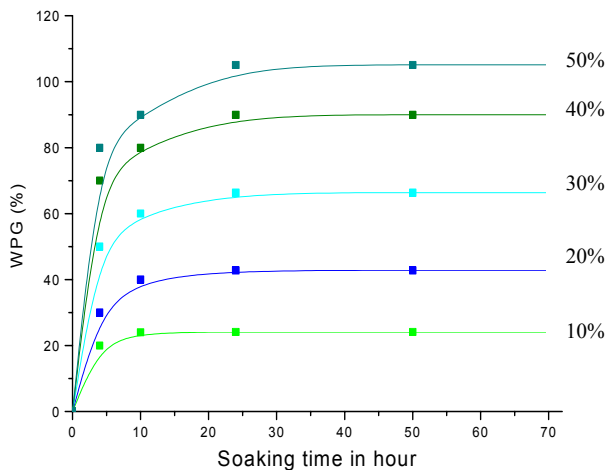
where SE is the volumetric swelling coefficient,  $V_1$  the volume of oven-dried sample before the water soaking test and  $V_2$  the wood volume after the test.

$$ASE = \frac{SE_2 - SE_1}{SE_1} * 100 \quad (4)$$

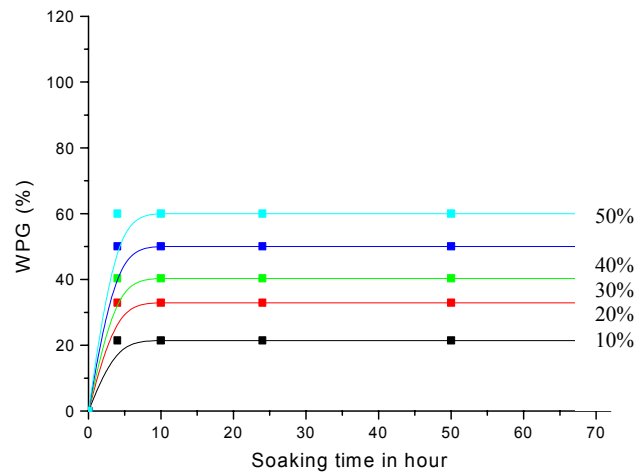
Where  $SE_1$  is the volumetric swelling coefficient for treated wood (ammonia-pretreated and not-ammonia pretreated) and  $SE_2$  is the coefficient for untreated wood.

## RESULTS AND DISCUSSION

The uptake of impregnating solution against soaking time for untreated and ammonia pre-treated wood samples are graphically shown in Fig.1 and Fig.2. The weight gain, in case of untreated wood samples, remains constant after 15-24 hours soaking while for ammonia pre-treated wood samples the impregnation is complete after 6-10 hours of soaking.

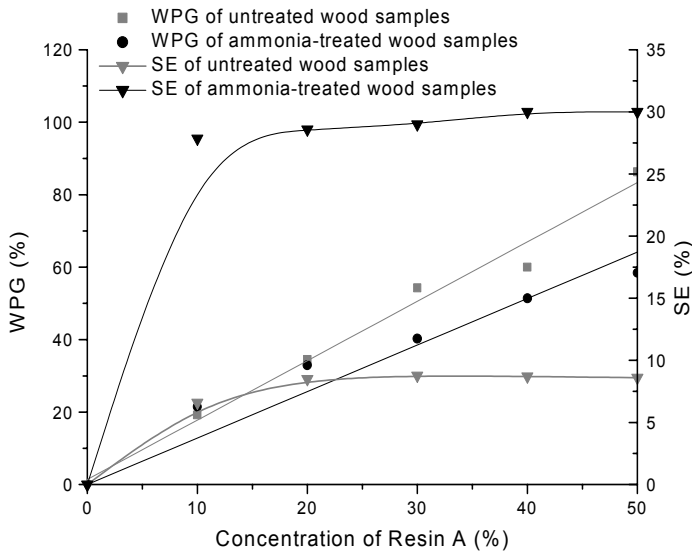


**Fig. 1:** Impregnation in vacuum against time of soaking of untreated wood in the Resin A aqueous solutions at different concentrations

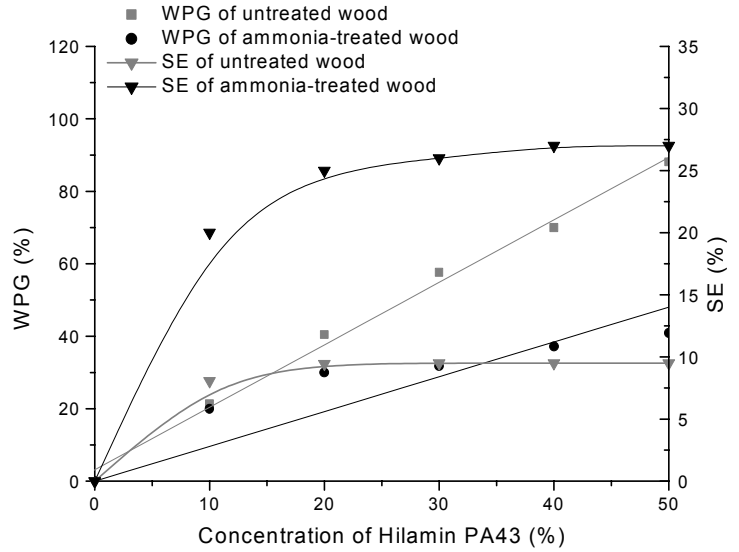


**Fig.2:** Impregnation against time of soaking of ammonia-treated wood in the Resin A aqueous solutions at different concentrations

Figures 3 and Figure 4 show the WPG and SE of wood + resin (Resin A and Hilamin PA43) and ammonia-wood + resin. In both cases, the WPG increases proportionately with increasing resin concentration, slowly in case of ammonia pre-treated wood samples. The SE shows a different behaviour: for wood+Resin A or wood+Hilamin PA43, the swelling efficiency reaches a maximum at 20% resin concentration, while for ammonia- wood+resin the maximum of SE occur at 30-40% resin concentration. Since in both of cases, the WPG continued to increase with increasing resin concentration, we can conclude that up to 20% for wood+resin respectively 30-40% for ammonia-wood+resin samples an excess of resin is stored in the lumen.



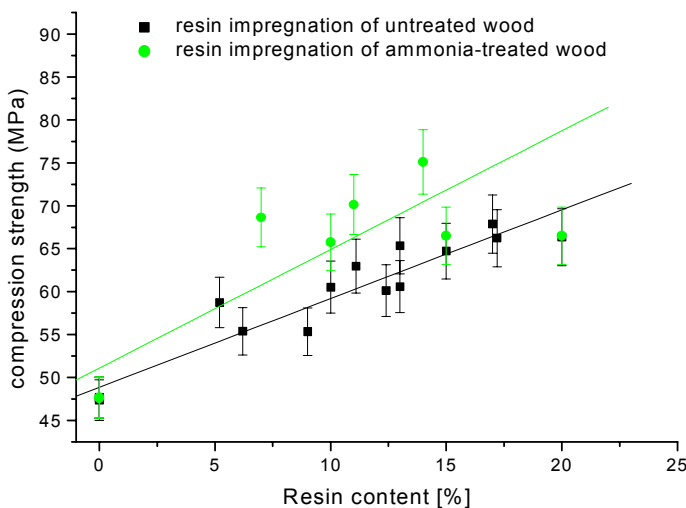
**Fig. 3: Weight percent gain and swelling efficiency resulting from increasing concentrations of Resin A. of Hil. PA43**



**Fig. 4: Weight percent gain and swelling efficiency resulting from increasing concentrations of Hilamin PA43**

The results show that the limited amount of resin deposited in the cell wall and acting as a bulking agent can be increased through an ammonia pre-treatment of wood (before the impregnation with resin and they crosslink).

Figure 5 shows that the compressive strengths determined from parallel tests on the fibres of ammonia-wood samples in the presence of Resin A and Hilamine PA43 were higher than those of the untreated-wood samples impregnated with the same resins. This result is to expect as long as the amount of resin deposited in the cell wall increased after an ammonia pre-treatment of the wood. There is no appreciable difference in compressive strengths depending on the kind of resin.



**Fig. 5: Compression strength versus resin content in untreated wood + Resin A and respectively Hilamin PA 43 and ammonia-wood + same resins.**

The water uptake capacity of cured samples of wood+resin and ammonia-wood+resin were determined through the swelling values after 24h of soaking in distilled water. These values were compared to those of the original, untreated samples. As is seen in Table 1 the samples that have

been previously pretreated with ammonia have shown an improved resistance to swelling in water compared to wood+resins, indicated by the values of ASE.

*Table 1: Swelling coefficient and antishrink efficiency (ASE) of wood+resin and ammonia-wood+resin samples*

Sample	% Resin	SE (%)	ASE (%)
Untreated wood		12,85	
Wood+ResinA	15	8,53	50,64
Ammonia-wood + Resin A	15	8,44	52,25
Wood+Hilamin PA43	13	9,45	35,98
Ammonia-wood+Hilamin PA43	14	8,82	45,69

## CONCLUSIONS

The pretreatment with ammonia of spruce wood samples leads to a reduction of the time necessary for a full impregnation with melamine resins to about a half compared to the impregnation time for untreated wood. It was also observed that the ammonia pretreatment increased the mechanical strength of the ammonia-wood+resin samples, compared to the untreated-wood+resin samples. This result is due in part, to the bulking effect of the resin in the cell wall. Ammonia pretreatment allows resins with higher concentration to penetrate into the cell wall. In case of lower concentration of resin, it can be presumed that the crosslinking is incomplete or does not occur due to the wide distribution of resin in the cell wall. This can also explain the improved resistance of the ammonia-wood+resin specimens to swelling on long-term exposure to water. Research is continuing to investigate the real extent of bulking effect of melamine resins in the cell voids.

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**SCALING UP AND MARKETS**  
ORAL PRESENTATIONS





## **Market Chances for Products Made of Modified Wood in German-speaking Markets**

Asta Eder

Competence Centre for Wood Composites and Wood Chemistry  
c/o: University of Natural Resources and Applied Life Sciences, Vienna  
Institute for Forest Sector Policy and Economics  
Gregor-Mendel-Straße 33  
A-1180 Wien  
Austria

Tel: +43-1-47654-4403 Fax:+43-1-47654-4407 E-mail:

**Keywords:** Markets for modified wood, applications for modified wood, producer survey

### **ABSTRACT**

Besides technical research focusing on modification of wood and its physical characterisation, market research is an important contribution to the entire research effort within the Austrian research program Wood Kplus. One goal of wood modification is product development. Therefore, promising market segments have to be identified in advance.

The preliminary survey results from the German-speaking markets for products made of modified wood are presented, especially markets for windows and doors, as well as parquet and wooden flooring. Comprehensive investigations of secondary data as well as representative surveys among decision makers and producers in Austria, Germany and Switzerland provide the data basis.

The secondary data studies cover market structures and quantities; the surveys assess market chances and potential new applications for products made of modified wood. The results of the surveys present the point of view of the producers and decision makers, who are responsible for the application of the products, for example architects.

According to the results, there are realistic market chances for modified wood, *e.g.* in the markets for windows and parquet flooring, given that the technical properties of modified wood meet the specific requirements of these product segments. In addition, analyses of the potential customers' willingness to pay extra costs due to the modification processes allow conclusions concerning price limits.

### **INTRODUCTION**

The Competence Centre for Wood Composites and Wood Chemistry (Wood Kplus) situated in Austria is specialised in research regarding wood composites and wood chemistry. Besides the technical research, market research for the wood composites is also an important part of the research efforts in the field of wood composites. The Institute for Forest Policy and Economics at the University of Natural Resources and Applied Life Sciences, Vienna, carries out the market research for Wood Kplus.

## EXPERIMENTAL METHODS

In the context introduced above, Wood Kplus conducted a survey among potential commercial customers (further producers) for modified wood in German-speaking areas in July 2002. This survey was part of a broad producer survey considering also other wood composites.

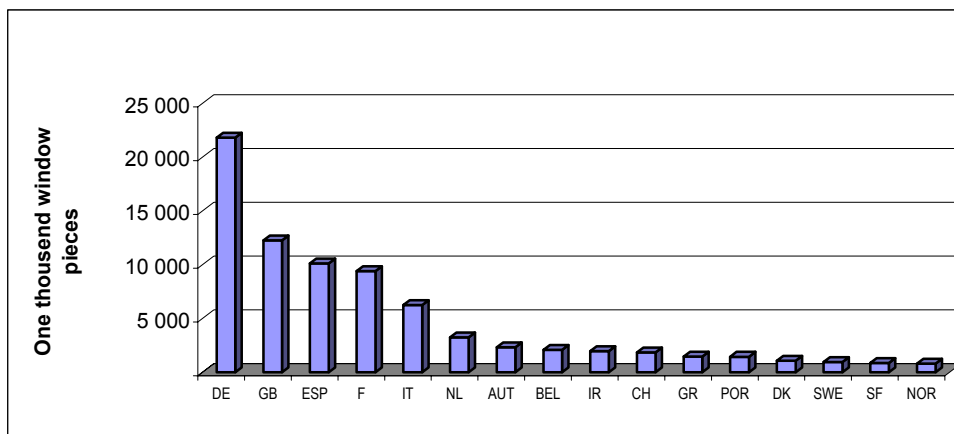
The target group for the surveys concerning modified wood in Germany, Austria and Switzerland were the producers of windows and doors, parquet and other wooden flooring, construction (producers of wooden and prefabricated houses) and furniture (office and home, kitchen, bath and garden). Among other things, the producers were asked to give their estimate regarding information status, interest, and potential applications for modified wood, as well as the willingness to pay. In the following, some preliminary results of the surveys from the windows and doors as well as parquet and wooden flooring sectors are discussed.

## RESULTS AND DISCUSSION

The results presented below only represent a small share of the rich information available from the surveys.

### *Window and Door Producers' Assessment of Modified Solid Wood*

The largest window market targeted by the survey is the German market (Fig. 1). The window market volume of Austria and Switzerland together only account for about 20 percent of the German market volume. The survey comprised all kinds of window producers typical for the German-speaking area (plastic, wood, aluminium and wood/aluminium). From a total sample number of 695 window and door producers, about 5 percent from each producer group responded.



*Figure 1: Market Sizes of the European Window Markets, Source: Weilharter H., 2001*

The development of the market shares of the different window frame materials in Germany can be seen in figure 2. Wooden windows in Germany and in the whole of Western Europe have dramatically lost their market share, especially to plastic windows. This is not only due to the lower price of the plastic windows, but also to the lower expenses on maintenance (Weilharter 2001).

Figure 3 shows the importance of criteria for the selection of window-frame material (continuous line) and the satisfaction with wooden windows (dotted line). Modification of wood would improve those technical features, which are seen as most important by decision makers for the selection of window materials.

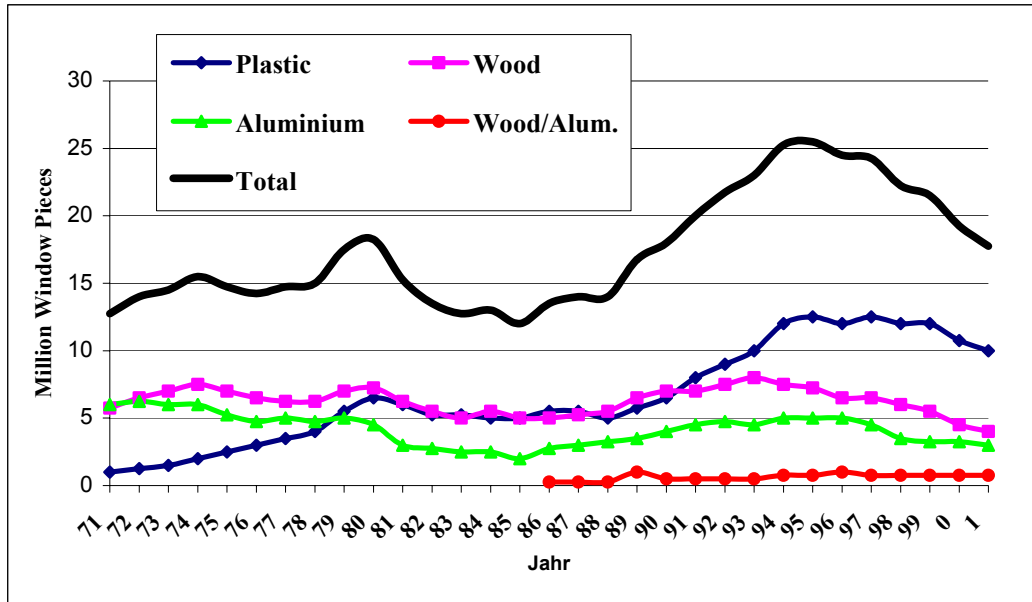


Figure 2: Development of the German Window Markets and the Window Frame Material, Source: Weilharter H., 2001

This is especially the case with durability and maintenance (Hogl and Schwarzbauer 2002). The results of the survey of windows producers confirm the importance of durability. The window producers were asked to rank the most important technical features for a good window-frame material. The three most important features named were product life, durability and water absorption behaviour.

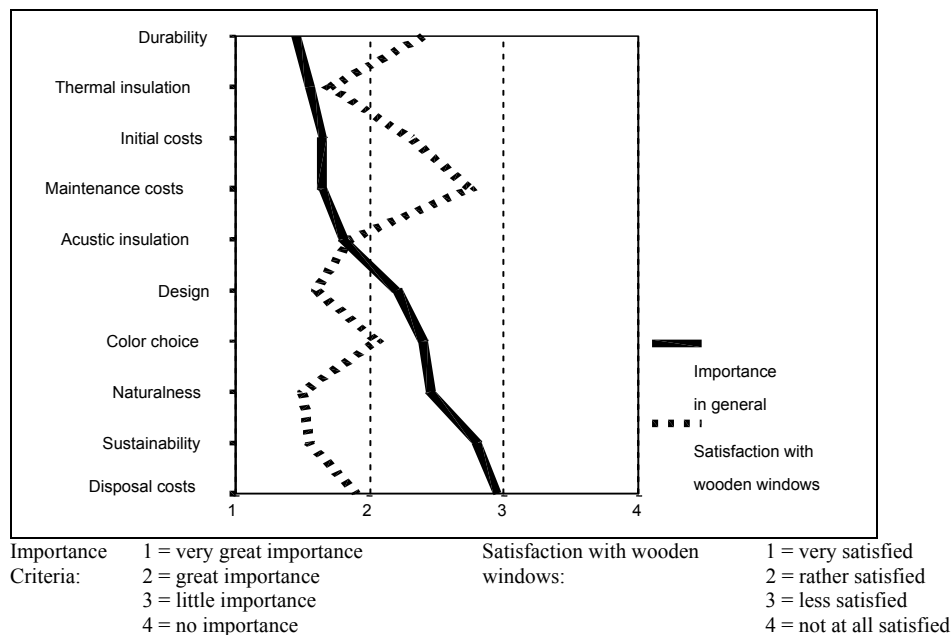
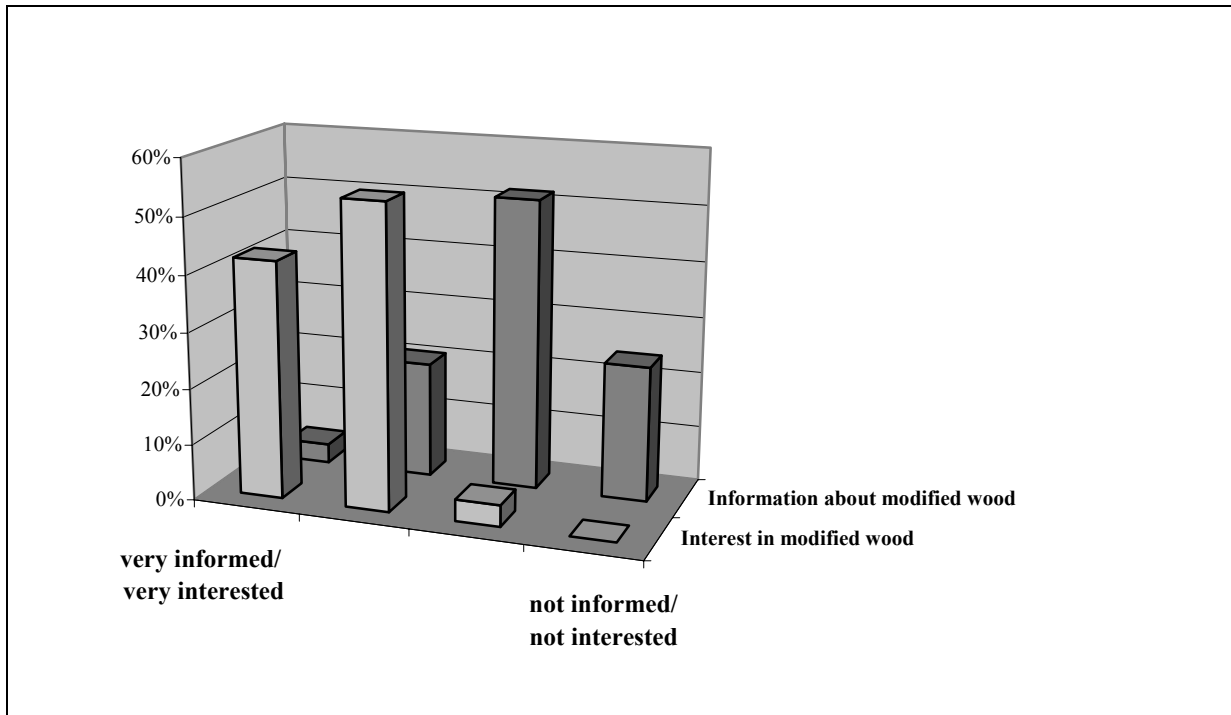


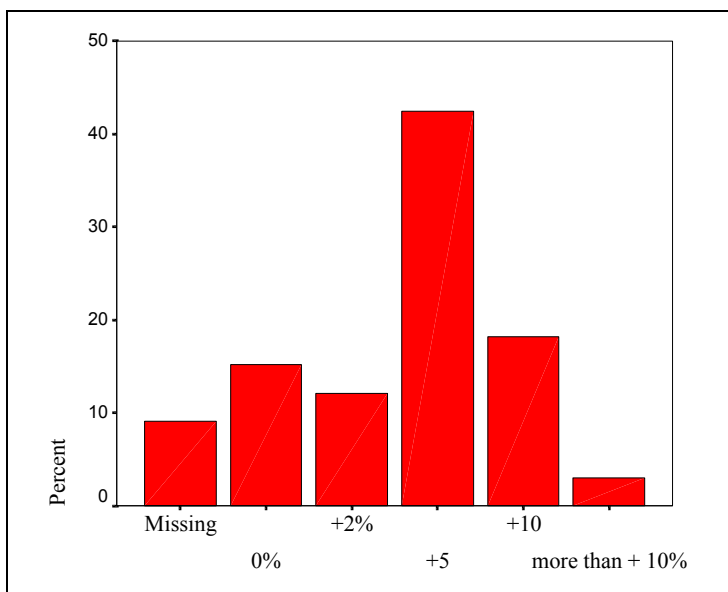
Figure 3: Importance of Criteria for the Selection of Window-frame Materials – Satisfaction with Wooden Windows, Source: Weilharter, 2001

The preliminary results of the window producer survey show that there is a lack of information about modified wood but indicate that the window producers are interested in modified wood (Fig. 4).



**Figure 4: Information about and Interest in Modified Wood (Percent of Respondents)**

An effort was made to measure the willingness to pay for modified wood with better technical properties than the usual wood raw material. Survey results concerning the willingness to pay should always be considered with caution, because it can be observed that the willingness to pay that is stated in a questionnaire does not necessarily represent reality. However, a trend in the direction to pay more for the raw material with better technical properties can be observed (Fig. 5).

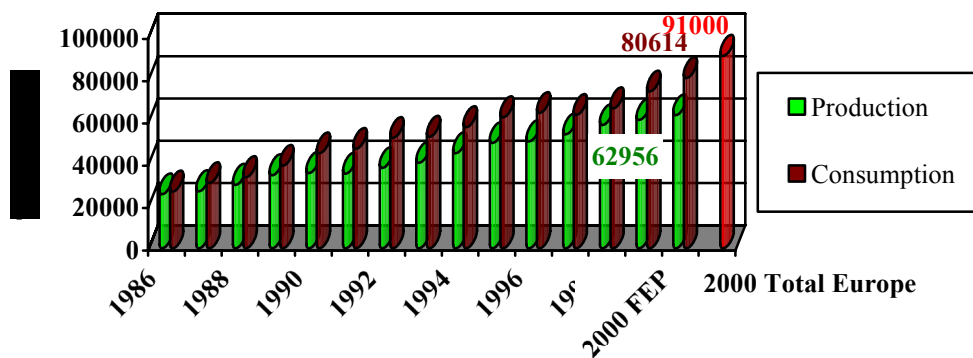


**Figure 5: Willingness to Pay for Modified Wood by Window Producers (Percent of Respondents)**

A price premium of five percent for modified wood with better technical properties would be accepted by more than 40 percent of the producers. Only less than 20 percent consider a price premium of 10 percent acceptable. On the other hand, only ten percent would not pay any price premium at all.

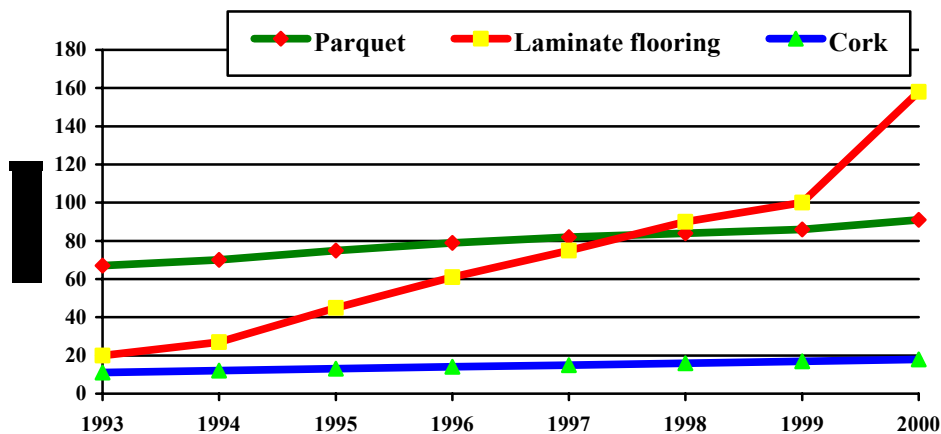
***Parquet and Wooden Floor Producers' Assessment of Modified Solid Wood***

The market share of parquet in 2000 is estimated at 5.3 percent of the total flooring market (EFP, 2002). Textile flooring has the biggest market share holding more than 50 percent in Western Europe. Figure 6 shows the growth of production and consumption of parquet in the countries represented by the Federation of European Parquet Industries (EFP). EPF-production accounts for approximately 88 percent of the total European Production, as can be seen in Figure 6.



*Figure 6: Development of the Production and Consumption of Parquet, Source: EFP, 2002*

An important competing material in the parquet market is laminate flooring. Figure 7 shows a larger increase of laminate flooring consumption in comparison to parquet. The market share of laminate flooring in 2000 amounted 5,9 percent and is only half percent larger than the market share of parquet.



*Figure 7: Consumption of Parquet, Laminate Flooring and Cork in Europe, Source: EFP, 2002*

Parquet production in the German-speaking countries amounts to about 30 percent of the total European parquet production as shown in figure 8. The survey of the parquet and wooden flooring producers covered 102 companies. 28 percent of them returned their questionnaire.

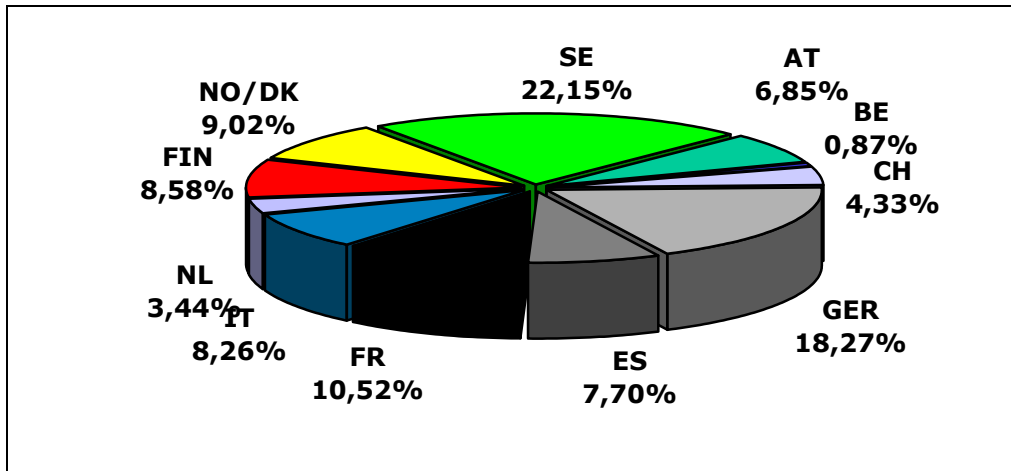


Figure 8: Production of Parquet in 2000 by Countries, Source: EFP, 2002

In order to assess the potential of modified wood as a raw material used for parquet, the parquet producers were asked about technical features, which are seen as important for parquet material. The four most important properties ranked by parquet producers were water absorption behaviour, form stability, optical appearance and durability.

A further task of the survey was to find more information about potential new applications for modified wood. That is why the parquet producers were asked: "In which applications would you consider using modified wood?" They were provided the option to give more than one answer. About 50 percent of the door producers would consider using modified wood in parquet production. Other answers of the parquet producers for the possible application of modified wood were e.g. construction (15%), outdoor applications, bathroom, façades (all 7%) (see figure 9).

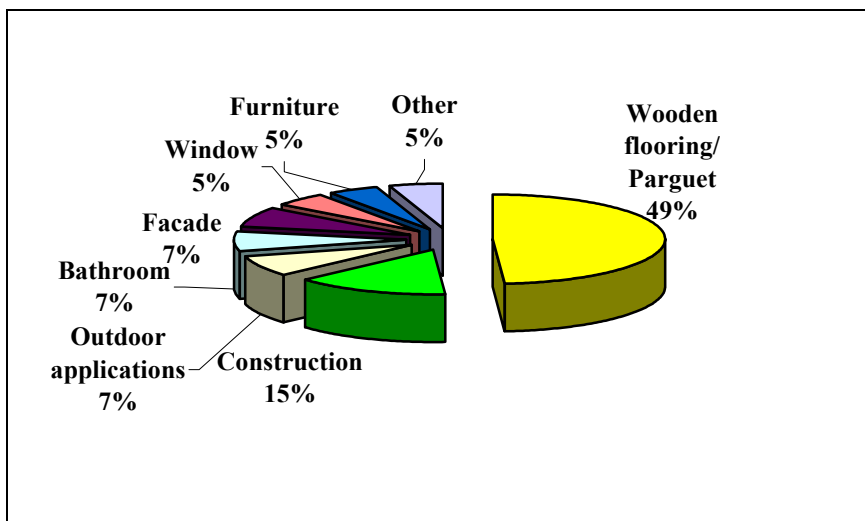
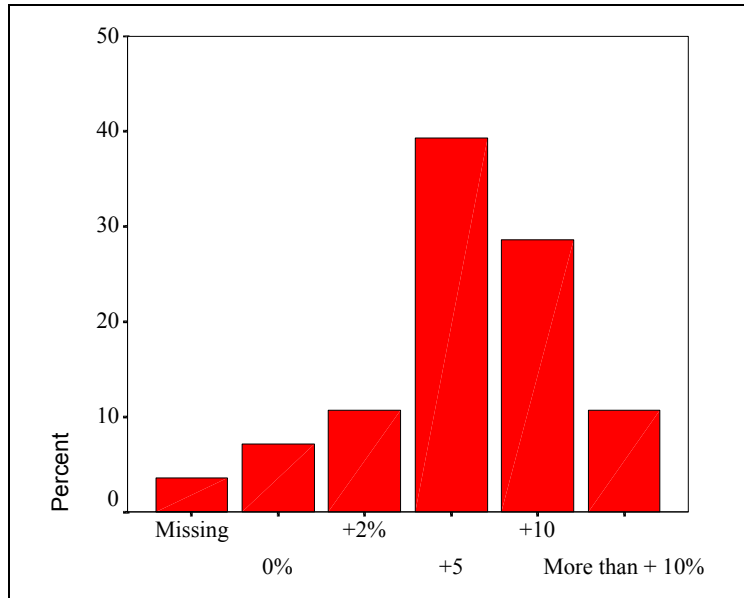


Figure 9: Potential Applications for Modified Wood from the Point of View of Parquet Producers (Percent of Respondents)

Another effort was made to assess the willingness to pay for modified wood with better technical properties than the usual wood raw material. As already mentioned above, the answers to the questions concerning the willingness to pay should be considered with caution. Figure 10 shows that up to 40 percent of the producers would consider a price premium of 5 percent for modified wood as compared to normal wood raw material. Approximately 30 percent consider a 10 percent price premium possible.



*Figure 10: Willingness to Pay for Modified Wood by Parquet Producers (Percent of Respondents)*

## CONCLUSIONS

If modification of wood can improve the technical features that are seen as important from the point of view of the producers in the various wood industry sectors, such as durability and maintenance for window producers or water absorption behaviour, form stability, optical appearance and durability for parquet producers, there are realistic chances for modified wood in these markets. There can also be observed a trend among the window and parquet producers towards paying more for the raw material with better technical properties. For enhancing market chances of modified wood more information must be available for the wood working industry. There can be observed a lack of information and at the same time an interest in modified wood on the part of by the window and parquet industry.

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## Furfurylation of Wood – Process, Properties and Commercial Production.

M Westin<sup>1</sup>, S Lande<sup>2</sup> and M Schneider<sup>3</sup>

<sup>1</sup> Swedish Institute for Wood Technology Research (Trätekt), Box 5609, SE-114 86 Stockholm, Sweden.  
E-mail address: mats.westin@tratek.se

<sup>2</sup> Wood Polymer Technologies ASA, NO-1596 Moss, Norway. E-mail address: sl@wpt.no

<sup>3</sup> University of New Brunswick and WoodTech Inc., 989 Clements Drive, Fredericton, New Brunswick, E3A 7J3, Canada. E-mail address: mhs@unb.ca

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### ABSTRACT

The first processes for “furfurylation” of wood (wood modification with furfuryl alcohol) were developed several decades ago. Furfuryl alcohol is a renewable chemical since it is derived from furfural, produced from hydrolysed biomass waste. Over the last decade modernised processes for furfurylation of wood have been developed. These new processes are based on completely new catalytic systems and process additives.

The properties of furfurylated wood depend on the retention of grafted/polymerised furfuryl alcohol (PFA) in the wood. At high modification levels (high retention of PFA) the enhancement of a wide variety of properties are achieved: an exceptional hardness increase, exceptional resistance to microbial decay and insect attack, high resistance to chemical degradation, increase in MOR & MOE, and high dimensional stability. At lower modification levels many property enhancements also occur, however to slightly lower extent. Notable are resistance to microbial decay and insect attack, increase in MOR & MOE, and relatively high dimensional stability.

Two main processes for production of furfurylated wood have been developed for WPT (Wood Polymer Technology ASA) by the authors – Kebony™ Dark (“Black technology”) for high modification level and VisorWood™ (“Brown technology”) for lower modification levels, where the name reflects the colour of the material produced by the process. Commercial production according to the *Kebony* process has been running since August 2000, mainly for flooring. A small *Kebony* production plant is now in operation in Lithuania. A larger *Kebony/VisorWood* production plant is planned to start up during the first half of 2003 in Porsgrunn, Norway. A plant operating according to the VisorWood process with an annual capacity of 15 000 m<sup>3</sup>, is most likely starting up in 2004, Norway.

Further commercialisation of the technology will be done through licences issued by WPT.

## INTRODUCTION

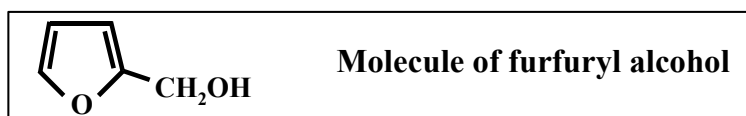
### *General introduction*

The early research with furfuryl alcohol (FA) concerned FA-resins as substitutes for phenol formaldehyde resins (PF resins) for adhesives, moulding compounds and inorganic composites. In the 1930's and 1940's several processes and patents concerning paper laminates, grinding wheels and metal casting moulds from FA resin impregnated paper or inorganic compounds such as silicon carbide, were developed (Dunlop and Peters 1953). Metal casting moulds and grinding wheels are still the main commercial applications for furfuryl alcohol. Research concerning modification of wood with furfuryl alcohol, hereafter referred to as "*furfurylation*" of wood, was initiated by the "pioneer of wood modification", Dr. Alfred Stamm, in the early 1950's. Most of the early work on wood furfurylation was done by his student, Irving Goldstein (Goldstein 1955, Goldstein 1960, Goldstein and Dreher 1960). Goldstein's process was based on zinc chloride as catalyst and mainly for application on wood veneers. He reported that treatment with 90% solutions of FA resulted in high dimensional stability, resistance to fungal decay and resistance to alkali and acids (Goldstein 1955, Goldstein and Dreher 1960). This research led to a small-scale production of *furfurylated* wood in the 1960's by Koppers Wood Inc. The products reported were laboratory bench tops, pulp mixer rotor-blades and knife handles (Kollman & Côté 1968, Stamm 1977). Focussing on the aesthetic properties, Williams (1971) developed a process for achieving mahogany-like products from cheaper woods treated with furfuryl alcohol resins. In the 1980's a Cuban researcher developed a process very similar to the Stamm/Goldstein process (Anaya 1984, Anaya 1987). However, this process was never commercialised.

A major problem with these processes is the catalytic systems used – zinc chloride has a devastating effect on the cellulose and thereby the long-term strength properties of the modified wood. More or less simultaneously, during the early 1990's, Schneider and Westin started research on new catalytic systems for furfurylation of wood, along similar paths of chemistry (Schneider 1995, Westin 1995, Westin *et al.* 1996). Both used cyclic carboxylic anhydrides, mainly maleic anhydride, as key catalysts. These novel systems lead to stable solutions with good impregnating properties and finally furfurylated wood with several outstanding properties, which will be presented in this paper. The properties of this novel type of furfurylated wood are in many respects superior to those of wood modified by the old Stamm/Goldstein process (Schneider 1995).

### *Chemistry of furfurylation of wood*

The acid catalyst reaction chemistry of furfuryl alcohol (FA) in wood is very complex. The result is a highly branched and cross-linked furan polymer grafted to wood cell wall polymers. However, the reaction parameters (catalyst type and concentration, pH, temperature, presence of water, etc.) highly affects the resulting product, *e.g.* degree of grafting, type of grafting bonds, dominating type of polymer units, and degradation of wood components (mainly hydrolysis of cellulose and hemicelluloses).



We suggest that the reaction types can be divided into a) homo-polymerisation of FA, b) co-polymerisation of FA and additives or wood extractive substances, and c) grafting of FA or PFA to wood cell wall polymers.

### Homo-polymerisation of FA

Early studies stated that the reaction speed is a simple function of pH in aqueous acid media (Dunlop and Peters 1953). However, there are several competing reactions and which one is dominating is affected by several other factors than the pH alone. Such factors are the temperature and presence of oxygen and weak organic bases. In the presence of powerful acid catalysts such as PTSA the dominating reaction is a very fast radical polymerisation with high degree of ring-opening reactions (Ekström 1980). However, these types of system are impossible to use as wood impregnation solutions, since they are not stable at room temperature. Impregnating solutions for wood must be stable during the impregnation process and then react readily when the wood is heated. In the initial phase of polymerisation with these types of stable system, there are two competing condensation reactions, illustrated in figure 1, reactions 1 and 2a (Choura *et al.* 1996, González *et al.* 1992). The reaction products according to reaction 1 usually dominate, and high reaction temperature and high FA concentration will further suppress the formation of ether bridges according to reaction 2a (González *et al.* 1992).

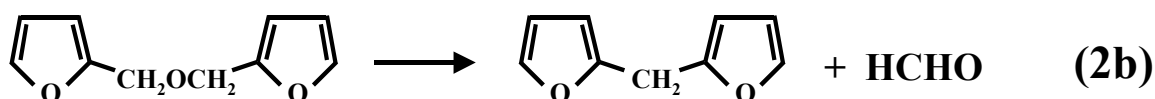
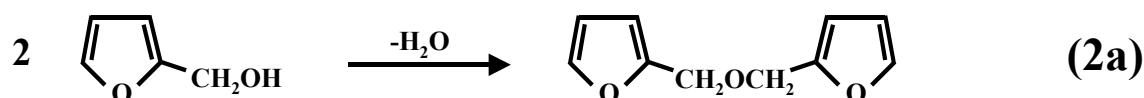
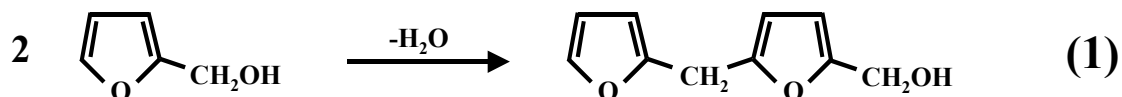


Figure 1: Initial polymerisation of FA (acid catalyst condensation reaction).

Since the ether-bridge of the resulting product in reaction 2a is unstable it is believed that this product undergoes reaction 2b, thus forming formaldehyde as intermediate by-product. It should be added that the terminal methylol group also could be split off as formaldehyde. The degree of this splitting depends on the temperature. Initially, a linear polymer is formed, but as the polymerisation progresses, cross-linking according to reactions 3 and 4 occurs more frequently and the polymer becomes infusible. It is believed that the formaldehyde formed according to reaction 2b and by splitting of terminal methylol groups, acts as cross-linking agent according to reaction 4. However, the dominating cross-linking reaction is by condensation reaction 3, given in figure 2. (Dunlop and Peters 1953, Choura *et al.* 1996, González *et al.* 1992)

It is also believed that some cross-linking in the late stages of polymerisation occurs through ring-opening reactions. A competing FA ring-opening reaction is the formation of levulic acid. This reaction and oxidation reactions can be suppressed by the presence of a weak organic base, *e.g.* triethanolamine (Delmonte 1949, Dunlop and Peters 1953). However, there were no significant differences in polymeric structure when the polymerisation was carried out in the presence of oxygen as compared to polymerisation under anaerobic conditions (González *et al.* 1992).

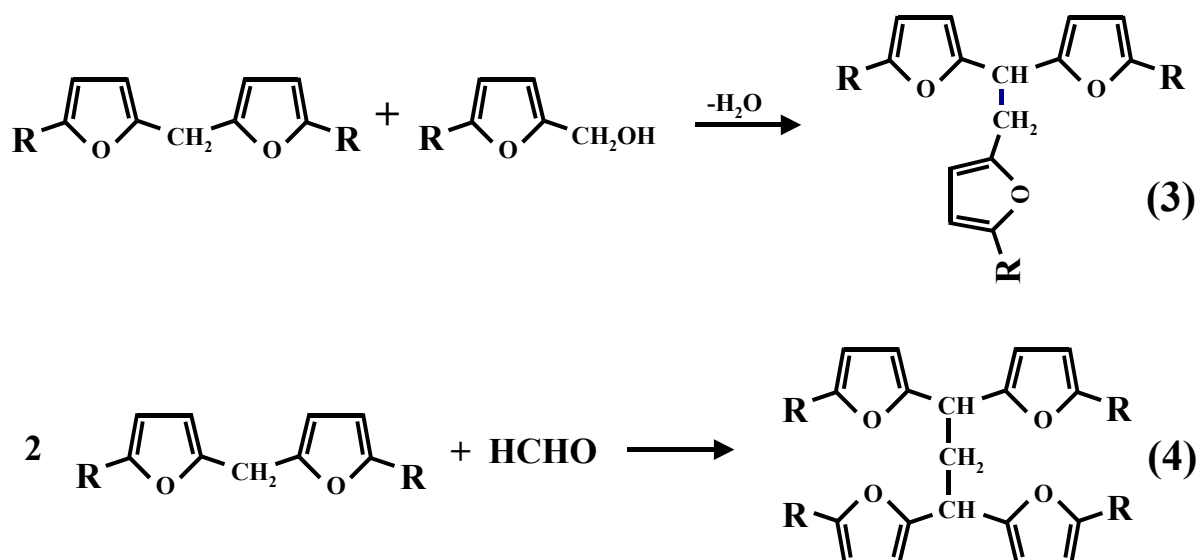


Figure 2: Cross-linking of FA-polymer chains.

### Grafting of FA to the wood cell wall components

Evidence of grafting reactions at an early stage of the polymerisation is the high degree of permanent bulking of the wood cell wall in the furfurylated wood. Similar to low-molecular PF-resins, FA impregnation leads to super-swelling of the cell wall – which means a slightly higher degree of swelling than water can achieve. However, as oligomers of PF become increasingly hydrophobic during the early stages of polymerisation, they begin to migrate out of the cell wall, which is the reason for a maximum anti-shrink efficiency of around 50% for PF resins. Since oligomers of FA are even more hydrophobic than PF-oligomers at the same DP, one would expect anti-shrink efficiencies below 50% for furfurylation of wood, but instead anti-shrink efficiencies of 80% can be achieved by furfurylation. This simple fact is strong evidence that grafting occurs at early stages of polymerisation – otherwise hydrophobic FA-oligomers would migrate.

Grafting of PFA onto cellulose has been shown possible by using ferric salts and peroxides as catalysts (Zavarin 1984). However, these types of catalysts cannot be used in stable impregnating solutions. Therefore, with the catalytic systems used in the process described in this paper, it is more likely to believe that grafting to hemicellulose and most of all to lignin is dominating. In figure 3 (reaction 5), a possible grafting reaction between FA and a guaiacyl unit of lignin (predominant in softwood lignins) is suggested.

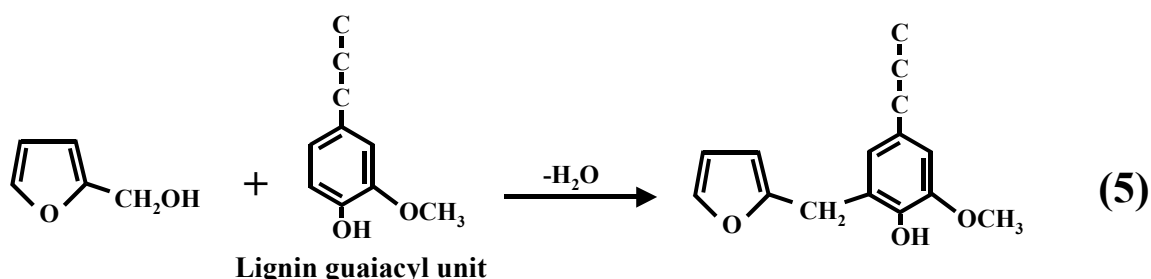


Figure 3: Suggested grafting reaction between FA and lignin unit

## INDUSTRIAL FURFURYLATION PROCESS

Wood Polymer Technology ASA (WPT) started the commercialisation process of furfurylation, based on the experiences and laboratory work carried out by Dr. Marc Schneider. The first task was to find a substitute material for the tropical hardwood Wengé. One main factor was the dark colour. Since furfurylated wood will achieve a dark or even black colour, this seemed to be a good modification system. Experimental work on suitable formulations was carried out in Canada and then later in Norway at Norwegian forest research institute, supervised by Dr. Schneider in 1998. Beech was chosen to be a suitable wood species, since beech is readily available in homogeneous qualities and is easy to treat. As much as 12 m<sup>3</sup> went through the laboratory before the process became a “blue print” and used for commercial production. However, due to high chemical consumption, this “high-furfurylated” product is bound to be expensive and designated for high-value niche products. The obvious way forward was to dilute the formulations and thereby reduce the amount of chemicals. One way to reduce the degree of furfurylation is by the use of a co-solvent, *i.e.* methanol or ethanol. This system will not interfere too much with the previous choice of catalytic systems. Westin used this strategy to investigate property changes with lowered weight percent gain. Industrially, such a strategy will lead to increased investments for the installation of proper solvent recovery equipment. Therefore, Schneider took another research route aiming at waterborne systems. However, the first trials with waterborne systems were not successful. The mix tended to separate almost instantly. Several new formulations including buffering agents and surfactants were tried and finally the trials lead to a successful water-based mixture. The process have now been adjusted for three different products with different ranges in degree of furfurylation: VisorWood<sup>TM</sup> (from softwood, WPG=20-30), Kebony<sup>TM</sup> (mainly from hardwoods, WPG=10-50) and Kebony<sup>TM</sup> Dark (from hardwoods, WPG ≥ 70). In the following the main process equipment, process parameters and plant design will be presented. A schematic plant design is presented in figure 4.

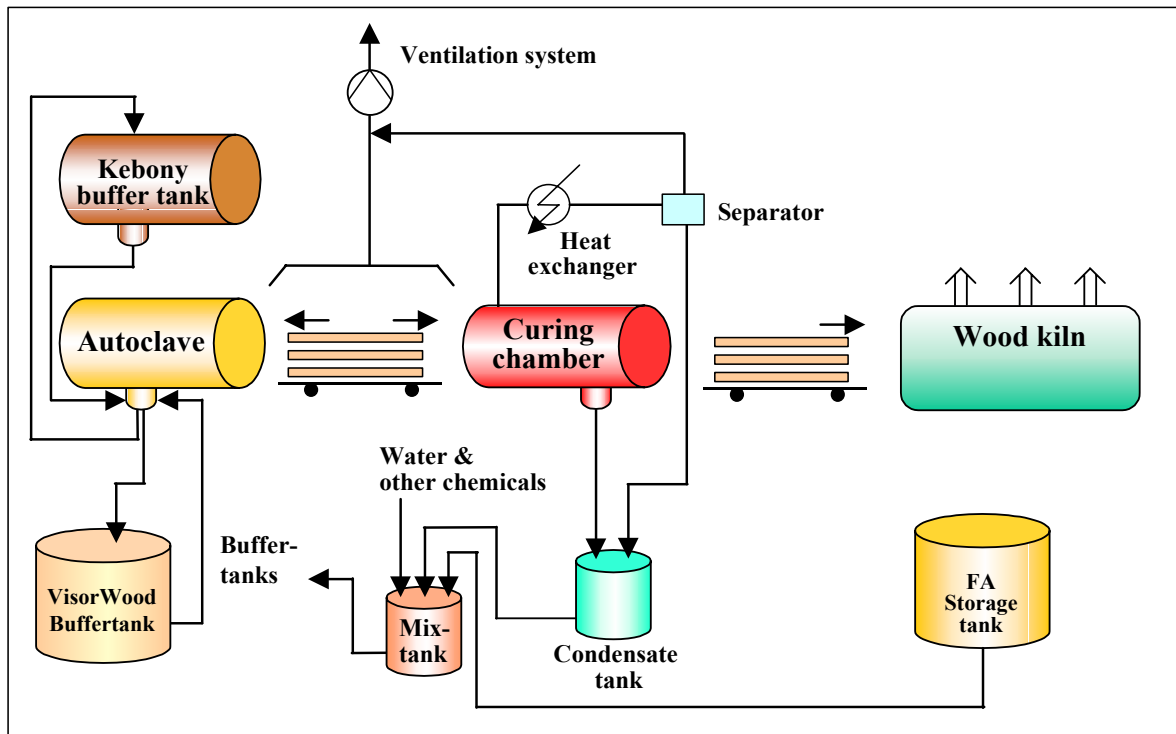


Figure 4: The WPT wood furfurylation process (schematic layout)

Impregnation of wood with the reactive treating solution is carried out in a rebuilt ordinary impregnation plant with concealed storage tanks. The same autoclave can be used for treatment with different FA-concentrations, if separate buffer tanks are used for the different solutions. A furfurylation plant will also need equipment for mixing the treating solutions. Therefore, a mixing tank with accessories to blend the FA with water, catalysts and stabilisers is included. There must be a curing step, a wood kiln to dry the wood and systems for recovery of heat and condensates from curing. Some of the working areas in addition to the chambers and kilns in the plant are ventilated. It is also important to keep FA emissions under control.

The process consists of the following steps (*cf.* with figure 4):

1. Storage and mixing of chemicals

The treating solutions are mixed in a separate mixing tank where different chemicals (FA, initiators/catalysts, buffering agents, surfactants and water) are added. The mixed solution is pumped to one of the buffer tanks. Condensate will be reused when mixing the water-based solution. Storage of furfuryl alcohol is located in a separate storage tank outside. The storage tank has a basin to prevent leakage to ground.

2. Impregnation (wood modification step1)

The timber is vacuum/pressure impregnated with the treating solution by the full cell process with a vacuum step for 30-60min, a pressure step at 10 bars for 2h and a short post-vacuum step.

3. Intermediate drying (step 2)

At lower modification levels, the treating solution is diluted by water and therefore an intermediate drying of the impregnated timber is needed before curing.

4. Reaction/curing (step 3)

An *in-situ* polymerisation of the chemicals and grafting reactions with the wood components occur during this process step. The curing chamber is heated with direct injection of steam for temperatures in the interval of 80-140°C depending of type of impregnation solution. The curing period is 6-8 hours. The chamber is operated as a closed system during the curing period, except for a ventilation period at the end. The ventilation gas is cooled with a heat exchanger and the condensate is separated from the gas in a separator. The condensate goes back to a condensate tank. Condensate from the chamber itself is pumped back to the condensate tank for reuse.

5. Drying

Final drying in a wood kiln is essential to minimise emissions and shipping dry lumber. For VisorWood material it will be necessary to reduce the moisture content after the curing period

6. Cleaning

The emissions during the process are taken care of in a cleaning process of ventilated gases.



**Figure 5: Part of the production plant**

## PROPERTIES OF FURFURYLATED WOOD

(Produced in laboratory pilot scale at Chalmers Univ. of Tech. or at WPT R&D centre)

All of the mechanical test results and most of the durability and physical test results presented in this section were produced within a national Swedish research project (Westin 1995) and a European research project (the “Chemowood” project, Fair-CT97-3187). The furfurylation procedure and test methods for those results are described in the paper by Epmeier *et al.* (2003) in this proceeding.

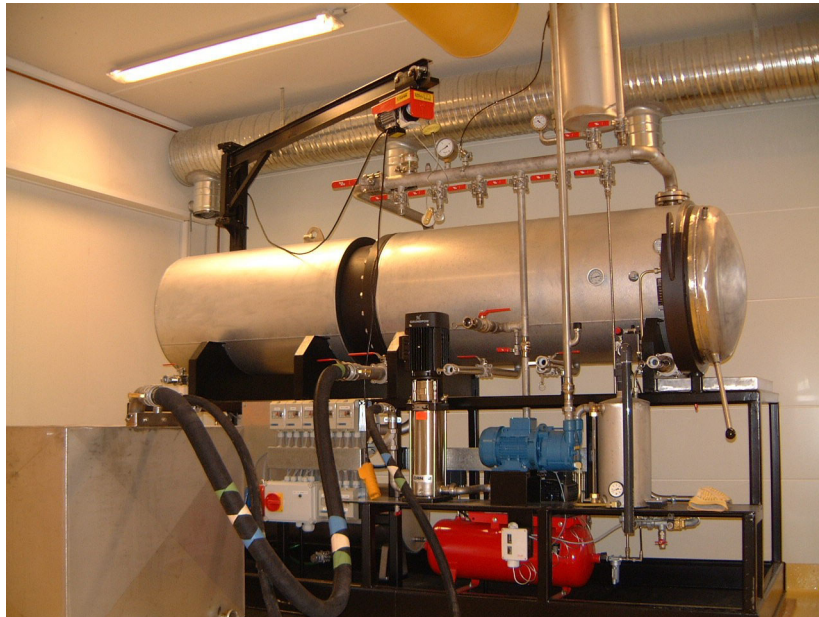
### *Materials and methods*

#### Wood materials

The main wood material used for the tests was Scots pine (*Pinus sylvestris L.*). For some of the tests furfurylation was also applied on beech (*Fagus sylvatica*) and birch (*Betula pubescens*). For termite field tests, two tropical wood species were included, agathis pine (*Agathis dammara*) and sengon (*Paraserianthes falcataria*).

#### Furfurylation of wood and preparation of test specimens

For the tests not described in Epmeier *et al.* (2003), the wood was treated in the industrial pilot plant of WPT in Moss, Norway, according to the process described earlier. These samples will be called *VisorWood* or *Kebony* in the following.



*Figure 6: Industrial pilot plant at the WPT R&D Centre in Moss. (The impregnation tube is composed of sections so that it can be used for 1,5m or 2,7m length of timber, depending on how many sections that are connected.)*

#### Test of emissions of volatile organic compounds (VOC's) to air

The testing procedure complied with the European testing standards ENV 717-1 (Wood based panels. Part 1: Formaldehyde emission by the chamber method, 1998) and ENV 13419-1 (Building products. Determination of the emission of volatile organic compounds – Part 1: Emission test chamber method. The test chamber (225 dm<sup>3</sup>, polished stainless steel) conditions were: 23°C, 45±3% RH, 1±0.05 h<sup>-1</sup> ventilation, air velocity of 0.1-0.3 m/s and panel loading was 1.0 m<sup>2</sup>/m<sup>3</sup>. Air samples were taken with a pump connected to a Tenax adsorption tube (for



VOC's) and Sep-pack-tubes (C18 polymers, coated with 2,4-dinitrophenylhydrazin for adsorption of aldehydes) after 3, 10 and 28 days. After elution with acetonitrile, aldehydes were analysed by HPLC with UV detection. The other VOC's were determined by thermal desorption of the Tenax and analysis by GC-MS. Quantification was carried out using internal standards.

#### **Test of emissions to water**

Furfurylated wood samples were leached according to EN 84. Leachate samples were taken from the first, three intermediate, and the final water exchanges and from the total cumulated leachate. The furfuryl alcohol and furfural content of the samples was analysed by HPLC.

#### **Fire test and analyses of smoke gases**

The fire tests were conducted according to ISO 5659-2 (tests in non-ventilated box) and ISO 5660-1 (cone calorimeter test, well ventilated scenario) and the smoke gases were analysed by GC-MS, GC-FID and FTIR spectroscopy.

#### **Testing of dimensional stability and mechanical properties**

For testing procedures, see Epmeier *et al.* (2003)

#### **Laboratory testing with pure basidiomycete cultures and terrestrial microcosms (TMC)**

Modified wood specimens (5x15x30mm) were exposed to monocultures of basidiomycetes for 16 weeks after which the percentage weight loss was calculated. The basidiomycetes were *Postia placenta* (brown rot fungus) and *Phanerochaete chrysosporium* (white rot fungus). The 5x10x100mm-specimens were buried to  $\frac{3}{4}$  of their length in the soil in three types of terrestrial microcosms, TMCs. These were: a compost soil (TMC 1), soil from the Simlångsdalen test field (TMC 2) and soil from a conifer forest (TMC 3). The characteristics conifer forest soil resembled the characteristics of the soil in the Ingvallsbenning test field. Specimens were removed after 12 months and the weight loss was calculated.

Experiments with radial growth for basidiomycetes on furfuryl-alcohol contaminated medium were also done. In these experiments the level of FA contamination of the growth media was 1000-4000 times higher than the highest concentration found in the EN 84 leachates. The basidiomycete strains included were two brown rot fungi: *Gloeophyllum trabeum* (Persson ex Fries) Murrill (BAM Ebw. 109) and *Coniophora puteana* (Schumacher ex Fries) Karsten (BAM Ebw. 15), and the white rot fungus *Coriolus versicolor* (Linnaeus) Quélet (CTB 863 A).

#### **Laboratory testing of resistance to termite attack**

Wafers, 1 x 1 x  $\frac{1}{4}$ -inch, cut from furfurylated wood (VisorWood and Kebony) were tested according to the AWPAs Standard Method E1-97 (AWPA 1999). Oven-dry wafers were placed on top of a 3x4 cm square of aluminium foil on the surface of 150g of damp silica sand (moistened with 30ml distilled water) inside a screw-top jar (8cm diameter, 10cm high). Formosan subterranean termites, *Coptotermes formosanus* Shiraki, were collected from an active field colony on Hawaii immediately before the laboratory test using a trapping technique. Four hundred termites (360 workers and 40 soldiers), with approximate natural caste proportions in field colonies, were added to each test jar. Each treatment was replicated five times. After adding termites, the jars were placed in an unlighted controlled-temperature cabinet at 28°C for 4 weeks. Each jar was inspected weekly for evidence of termite activity in the soil and on the test materials. At the conclusion of the 4-week test period, percentage termite mortality was recorded, the wafers were rated visually according to a 0-10 scale (where 10 is sound, 9 is light

attack, 7 is moderate attack and penetration, 4 is heavy attack, and 0 is total failure of the wood sample), and the oven-dry weight change was recorded for each wafer.

### **Field tests**

Field tests in soil contact in three Swedish fields, two Indonesian fields with subterranean termite activity and in a marine environment according to EN 275 and a modified version of EN 252 were carried out. These tests are further described in Epmeier *et al.* (2003).

### ***Results and discussion***

#### **VOC emissions to air from freshly produced VisorWood**

The total VOC from VisorWood was low and well below odour threshold limits in all cases. The major component was furfural, but the emissions of this compound are reduced to less than ¼ after one month. The same pattern was seen for most other detectable compounds except furfuryl alcohol, which is emitted at a constant (however low) level during the testing period. (see table 1)

*Table 1: The volatile organic compounds detectable in GC-MC analysis*

Compound	Concentration	Concentration	Concentration	Threshold value odour (µg/m <sup>3</sup> )
	Climate chamber 3 days (µg/m <sup>3</sup> )	Climate chamber 10 days (µg/m <sup>3</sup> )	Climate chamber 28 days (µg/m <sup>3</sup> )	
Furfural	214	107	47	
Furfuryl alcohol	50	?	60	
Tetrahydrofuran-methanol	44	25	13	
Toluene	30	16	9	
Furandiene	18	5	-	
Benzene/alcohol	15	4	2	
Benzaldehyde	8	3	1	186
Hexanal	7	3	2	58
Xylene/ethylbensene	6	2	-	214
α-pinene	3	1	1	3890
Methylcyclohexane	3	1	-	High
Butyl acetate	3	1	1	47
MIBK/hexanone	1	1	1	540 (MIBK)

#### **Emissions from VisorWood to water during EN 84 leaching**

The average concentration of FA in the leachate was 0.23 mg/l. The initial concentration (first exchange) was slightly higher and the final slightly lower. If any furfural was present, it was well below detection limit (0.05 mg/l) of the HPLC analysis.

#### **Performance of VisorWood in fire testing**

In the non-ventilated combustion oven the results for VisorWood was similar to the results of untreated wood, except for a reduction in mass loss and production of smoke gases (almost 50% lower specific optical density of the smoke). In the cone calorimeter test, VisorWood had the same time to flame extinction, and the same effective heat of combustion values as untreated wood. However, the heat release rate, total heat released and mass loss was lower for VisorWood than for untreated wood.

The total amount of VOC produced from VisorWood was approx. 50% lower than from untreated wood in the non-ventilated combustion oven test. In the cone calorimeter they were 25% lower. The total amount of polyaromatic compounds produced was also significantly lower for VisorWood.

### Mechanical and physical properties

The volumetric ASE is high, even at low levels of furfurylation – at WPG=32 (weight percent gain) the ASE is close to 50%, at WPG=47 the ASE is approx 70% (see striped bars in Figure 6). The stiffness stabilisation efficiency (SSE, grey bars in figure 6) is also high, already at moderate degrees of furfurylation and is only slightly lower than the ASE values. The hardness increase is moderate at low WPGs but very high at high WPGs. The drawback is the decreased impact bending strength at medium to high WPGs (negative bars), although the drastic reduction shown by the bars in the diagram is to some extent an artefact of a sample size much smaller than the standard specifies. In other impact bending tests of VisorWood and Kebony with correct test specimen size, the results show more modest reduction of impact strength (see table 8)

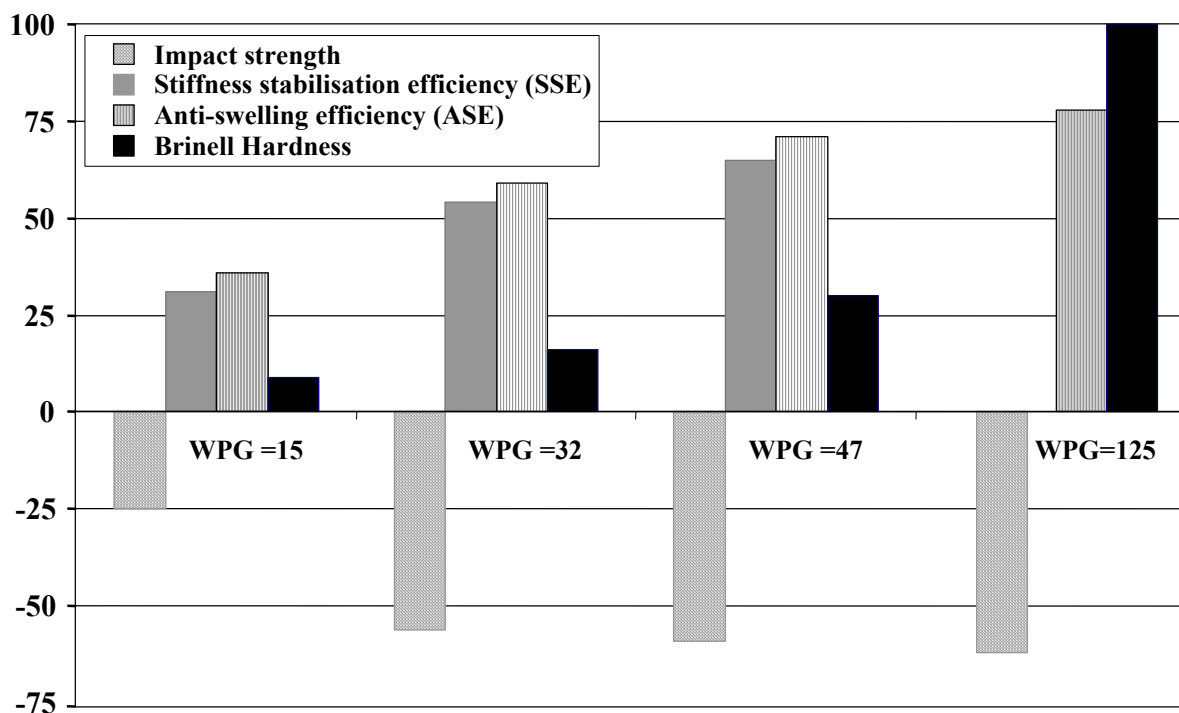


Figure 6: Mechanical and physical properties of furfurylated wood as a function of modification level

### Laboratory tests with pure basidiomycetes cultures

The results from testing in bioassays with pure brown rot and white rot fungi can be seen in the right-hand columns (weight loss caused by *Postia* and *Panerochaete* respectively) of table 2. The weight loss (WL) values of medium- and high-furfurylated wood samples by brown rot decay are lower than the WL value of CCA-treated samples. Only for the low-furfurylated samples the WL values are slightly higher than for CCA-treated samples. The WL of the controls by white rot decay was rather low, especially in the set-up with CCA-treated samples. However, the conclusion is that the resistance to white rot decay is also high for the furfurylated wood.

**Table2: Results in laboratory bioassays with pure basidiomycetes cultures**

Modification level		Weight loss after 16 weeks in Bioassay 1 (brown rot) <i>Postia placenta</i>	Weight loss after 16 weeks in Bioassay 2 (white rot) <i>Phanerochaete chrysospor.</i>
		(%)	(%)
<b>Control I</b>	untreated	48.3	22.7
<b>Furfurylated 1</b>	WPG = 25	9.2	4.5
	WPG = 125	1.7	2.4
<b>Control II</b>	untreated	65.6	24.2
<b>Furfurylated II</b>	WPG = 23	6.9	5.0
	WPG = 128	1.1	2.9
<b>Control III</b>	untreated	60.0	20.0
<b>Furfurylated III</b>	WPG = 35	4.3	-
	WPG = 75	4.3	-
	WPG = 120	2.4	2.7
<b>Control IV</b>	untreated	44.1	15.2
<b>CCA</b>	9 kg/m <sup>3</sup>	4.0	1.1

### **Radial growth of basidiomycetes on FA-contaminated growth media**

Although the concentration of furfuryl alcohol in the growth media was a 1000-4000 times higher than the concentrations in EN 84 leachates, there was no inhibitory effect on the radial growth of any of the basidiomycetes tested.

### **Laboratory tests with terrestrial microcoms (TMC)**

**Table 3: Results for furfurylated wood after 12 months in 3 different TMCs.**

Modification type (/chemical)	Modification level	Weight loss during leaching %	Weight loss (%) in TMC 1 (Compost soil) 12 months expo	Weight loss (%) in TMC 2 (Simlångsdalen soil) 12 months exposure	Weight loss (%) in TMC 3 (Conifer forest soil) 12 months exposure
<b>Pine Control I</b>	untreated	2.4	78.0	62.9	20.1
	Acetone-extracted	2.1	76.7	58.5	14.8
<b>Furfurylated pine</b>	WPG = 22	2.4	5.7	5.2	8.5
	WPG = 41	1.7	2.1	2.8	5.0
	WPG = 60	0.6	1.0	1.8	1.9
<b>Pine Control II</b>	untreated	not leached	73	51	57
<b>VisorWood</b>	WPG = 25	not leached	7	3	4
<b>Pine Control III</b>	untreated	not leached	94.5	41.9	17.1
<b>CCA (NWPC-Standard no.1)</b>	4 kg/m <sup>3</sup> (class AB)	not leached	42.8	5.4	2.9
	9 kg/m <sup>3</sup> (class A)	not leached	25.2	2.1	1.3
<b>Birch Control</b>	untreated	1.5	85.8	30.0	28.2
<b>Furfurylated birch</b>	WPG = 40	1.6	5.6	6.6	7.1

The results from TMC testing in three types of soils can be seen in the right-hand columns (weight loss caused by decay) of tables 5 and 6. Prior to the test the samples were leached and the resulting weight losses can be seen in the third column. There was no significant difference between the untreated and the acetone extracted pine sapwood. There were only minor differences found between the weight losses from leaching of the control samples and leaching of the modified samples (see 3<sup>rd</sup> column of table 3).

### **Resistance to termite attack in laboratory tests**

For untreated pine the average weight loss was 66% and the AWPA rating 0 (total failure). For untreated beech the average weight loss was 38% and the AWPA rating 4.0 (severe attack). For pine VisorWood, the average weight loss was 8% and the AWPA rating 7.4. However, for beech VisorWood, the average weight loss was only 2% and the AWPA rating 9.6. Finally, for beech Kebony, the average weight loss was 8% and the AWPA rating 7.8. For approval of a treatment as completely effective against termite attack a visual rating of at least 7 is required. This requirement is fulfilled in all three groups of furfurylated wood. However, the maximum single weight loss accepted is 5% with a maximum average of 3%. This criteria was only fulfilled by the beech VisorWood group. Thereby, the general conclusion is that furfurylation provides strong (although not complete) termite resistance.

### **In-ground field tests with mini-stakes in Sweden**

A comparison of the performance of furfurylated wood mini-stakes in Simlångsdalen with the performance in Ultuna and Ingvallsbenning is shown in Table 4. Although the decay type is very different in these three fields, the performance is quite similar in all three fields. At the higher modification levels furfurylation seem to provide a performance equal to or better than CCA in the retention level approved for use in HC4, 9 kg/m<sup>3</sup> (based on crystal water free salt, which corresponds to 12 kg/m<sup>3</sup> based on preservative product).

*Table 4: Condition of pine sapwood mini-stakes (8x20x200mm) after 7 years in three Swedish fields.*

Chemical treatment	Chemical retention		Index of Decay (0-100% decay)		
	WPG	(kg/m <sup>3</sup> )	Simlångsdalen	Ultuna	Ingvallsbenning
Furfurylation	15		75	58	67*
	33*		31*		
	50		12	17	12*
	>100		0	0	0*
NWPC <sup>a</sup> Standard No.1 (CCA)		2.1 <sup>b</sup>	88	96	84*
		9.0 <sup>b</sup>	21	54	3*
Untreated controls	-	-	100	100	100*

<sup>a</sup> Nordic Wood Preservation Council    <sup>b</sup> CuO (19 wt-%); CrO<sub>3</sub> (36 wt-%); As<sub>2</sub>O<sub>5</sub> (45 wt-%)    \* Five years exposure

### **In-ground mini-stake tests in fields with high subterranean termite activity**

The performance of high-furfurylated wood was very good – all these stakes were sound after one year in the Bogor field whereas very little of the control stakes remained (93-98% weight loss). In a supplementary test in the Bandung field, medium-furfurylated pine (WPG=43) also seems to be resistant to termite attack. (See table 5)

**Table 5: Performance of mini-stakes (8 x 20 x 200 mm) in the Indonesian termite fields**

Modification level		Bogor field, Weight loss (%)			Bandung field, Weight loss (%)		
		3 months	6 months	1 year	3 months	6 months	1 year
Scots pine Control		33	47	93	10	66	85
Furfurylated pine	- WPG = 15	3	16	62	4	62	65
	- WPG = 43	-	-	-	0	0	0
	- WPG =115	1	1	2	0	0	0
Agathis pine Control		36	70	95			
Furfurylated agathis	- WPG = 15	2	2	61			
	- WPG =115	0	1	2			
Sengon Control		16	85	98			
Furfurylated sengon	- WPG = 15	2	9	85			
	- WPG =115	0	1	1			

**Marine field tests (EN 275)**

All untreated pine sapwood samples in the first set of controls were rejected at the assessment after one year (see table 7, column to the right). They were so heavily attacked by *Teredo navalis* (shipworms) that the *teredo* tunnels covered more than 90% of the X-ray pictures. They were replaced with new controls and at each assessment during the forthcoming years all controls had failed due to *teredo* attack and were replaced. However, the furfurylated samples at medium to high modification level were all rated sound after 3 years of testing.

**Table 7: Condition of pine sapwood samples (25 x 75 x 200 mm) after 3 years of exposure on test rigs in the bay outside Kristineberg Marine Research Station.**

Wood treatment chemical	Chemical retention		No. of stakes	No. of samples classified as			Rating, Terenid attack (0-4)	Overall rating	Aver. Service life (years)
	WPG	(kg/m <sup>3</sup> )		sound	attacked	rejected			
Furfuryl alcohol (Falc)	11		5	-	5	1	3.0	Severe	-
	29		5	5	-	-	0.0	Sound	-
	50		5	5	-	-	0.0	Sound	-
	120		5	5	-	-	0.0	Sound	-
CCA (NWPC <sup>a</sup> Standard No.1)		4 <sup>b</sup>	6	-	1	5	3.8	Failed	-
		18 <sup>b</sup>	6	6	-	-	0.0	Sound	-
Untreated pine sap controls	-	-	8+5+5	-	-	8+5+5	4.0 <sup>c</sup>	Failed <sup>c</sup>	1.0 <sup>c</sup>
Untreated <i>Minquartia g.</i>	-	-	5	5	-	-	0.0	Sound	-

<sup>a</sup> Nordic Wood Preservation Council    <sup>b</sup> CuO (19 wt-%); CrO<sub>3</sub> (36 wt-%); As<sub>2</sub>O<sub>5</sub> (45 wt-%)

<sup>c</sup> Three sets, each lasted 1 year

**INDUSTRIAL PRODUCTION AND APPLICATION**

Today the main user of furfurylated wood, Boen AS, produces Kebony under a license agreement granted by WPT in Lithuania. The main end product is shipdeck-style parquet flooring. There are three main brands of furfurylated wood products, marketed by WPT: VisorWood, Kebony and Kebony Dark.

## *Application areas*

### **1. VisorWood**

Furfurylation of lumber for rough outdoor application. The technology is suitable for outdoor uses where resistance against decay, dimensional stability, stable weathering properties and/or paintability properties are of importance. Examples of application areas are: Decking, marine applications, façade cladding, window joinery, thresholds, poles, wooden roofs and other building material. Degree of furfurylation is typically in the range of WPG 20% - WPG 40%. Main wood species is Scots pine.



*Figure 6: Roof made of pine VisorWood.*



*Figure 7: Decking made of pine VisorWood.*

### **2. Kebony**

The technology is suitable for indoor uses and high value outdoor applications where dimensional stability and an attractive golden brown appearance are of importance. A target indoor area is flooring. For outdoor use, target products are furniture, boat decking and decorative joinery. The degree of furfurylation can vary in a wide range from WPG 10% to WPG 50%. Additional colouring systems might be added to the treatment to achieve even more attractive appearance. Typical wood species for treatment will be European maple, birch and beech.

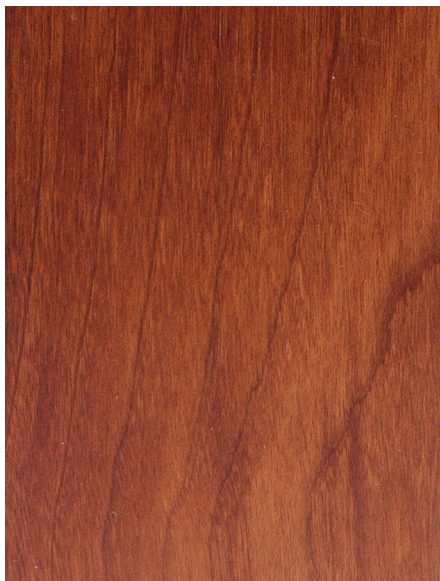


Figure 8: Maple Kebony

Figure 9: Garden table of birch Kebony

### 3. Kebony Dark

Kebony Dark has proven its outstanding qualities in hardness, dimensional stability, appearance and colour stability through commercial use for more than two years. The technology has been commercialised as a substitute to the very expensive tropical hardwood Wengé. Key areas are flooring, design furniture and decorative uses. The degree of furfurylation might vary upon the density of the wood species, but will typically be in the high range of WPG 70% to WPG 100%. Typical wood species for treatment will be birch and beech.



Figure 9: Birch Kebony Dark.

Figure 10: Intermediate layers of beech Kebony Dark In shipdeck-style parquet flooring.

To describe the different technologies an attempt is made to compare each of them in table 8.

Table 8: Comparison of furfurylated wood products

Properties	Untreated wood*	VisorWood	Kebony	Kebony dark	Unit
<b>Physical</b>					
Density	0.4-0.7	+ 20-30%	+ 15-35%	+ 50-100%	g/cm <sup>3</sup>
Colour	Light/yellow	brown	Brown/redish	Dark brown/black	
Dimensional stability	0	25-40%	35-50%	75-90%	ASE
Hygroscopicity	100%	75%	50%	10%	
Color-fastness	-	Good	Good	Very Good	
Glueability	-	As for untreated	As for tropical hardwood	As for tropical hardwood	
Surface treatment	-	As for untreated	As for tropical hardwood	As for tropical hardwood	
<b>Durability</b>					
Estimated durability class	natural	4-5	2	1-2	1
For Hazard classes		1-3	3-4	3-4	4-5
<b>Mechanical</b>					
Compres. // to grain	50-60	50-60	55-65	100	Mpa
Impact bending	50-100	- 20%	-20%	- 40%	KJ/m <sup>2</sup>
Hardness	2-6	3-7	4-7	9	Brinell
Workability	-	As for untreated softwood	As for untreated hardwood	As for tropical hardwoods	
<b>Environmental</b>					
Deposit	-	As for untreated	As for untreated	As for untreated	

\* Wood - represents Western Europe softwoods and hardwoods



### ***Commercialisation strategy***

WPT shall be a leading company in developing technologies for wood modification which give treated products enhanced durability, strength and hardness. This shall be achieved through continued research & development and commercial competence.

The business concept is based on selling/licensing the technology to the wood treatment industry. WPT will enter into production in special cases only.

WPT will promote the three brand names in relation to the technologies; VisorWood, Kebony and Kebony Dark.



# ***Kebony***

WPT's market strategy is to:

*1. Create environmental awareness and establish end-product demand.*

WPT will contribute to create environmental awareness and maintain continuous liaison with the authorities. WPT is working closely with end product producers in a wide range of application areas.

*2. Market technologies and offer licenses.*

WPT's major objective is to market its technology and issue production licences. WPT is working closely with impregnation plants and other end product producers. WPT's main focus is currently to promote its technologies and products in Europe.

WPT is also marketing its technologies and products through interest organisations for the wood preservation companies, environmental organisations, R&D establishments and governmental institutions.

### ***Production capacity***

Currently, Boen AS is producing Kebony Dark at their plant in Lithuania under a production license from WPT.

WPT has decided to establish the first large production plant for furfurylation of wood with WPT's processes for VisorWood, Kebony and Kebony Dark. The plant will be operated by the new production company, *WPT Products*. WPT Products will meet initial demands from customers, of which two are industrial partners in the production company. The two partners

have interests in the flooring and the decking market. The plant will be located at Norsk Hydro's industrial park at Porsgrunn. WPT Products will operate under a production licence from WPT.

The production will initially have a production capacity of 5.000 m<sup>3</sup>/year, and focus on the following applications: Parquet flooring, thresholds for exterior doors, decking/sea ports and wooden roofs.

A plant operating according to the VisorWood process with an annual capacity of 15 000 m<sup>3</sup>, is most likely starting up in 2004, Norway.

## CONCLUSIONS

The authors have successfully developed new processes for furfurylation of wood. The furfurylation can provide several outstanding properties:

- High dimensional stability – up to 90% ASE
- Highly increased hardness – up to 9 in Brinell hardness
- High durability – performance equal to or better than CCA-treated wood in field tests
- Strong resistance to termite attack and marine borers
- Better performance during fire – less smoke production
- Attractive aesthetic appearance – “tropical wood”-like

High-furfurylated wood has been produced commercially for two and a half years using the WPT process and a larger production of furfurylated wood is planned to start before the end of this summer. WPT will further commercialise the technology through licenses.

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## **Thermoplasticisation of Wood by Chemical Modification, a Possible Novel Way to High Performance Wood Composites and Alternative Technologies**

Maria Cristina Timar

“Transilvania” University of Brasov, Department of Wood Technology,  
29 Eroilor Street, 2200 Brasov, Romania, e-mail: timar@artimar.ro

**Keywords:** thermoplasticised wood, wood-fibre/plastic composites, physical and mechanical properties, self-protected solid wood, biological resistance

### **ABSTRACT**

Wood properties may be engineered by chemical modification, as a direct consequence of the correlation between chemical structure of wood and its properties. Wood with thermoplastic properties can be prepared by adequate chemical modifications. The paper presents a short insight into the basics of thermoplasticisation of wood by chemical modification alongside with some research results highlighting ideas of possible applications.

Aspen sawdust was chemically modified in a two-step procedure to impart thermoplastic properties. Plastic-like composite boards were obtained by the compression moulding of the thermoplasticised wood material. These are a novel type of wood-fibre/plastic composite in that partial melting of the chemically thermoplasticised wood generates the matrix, and the remaining unmelted wood functions as a reinforcing material. These composites show very interesting physical, mechanical and biological properties. They are water-resistant and dimensionally stable materials that display good electrical insulating behaviour. Their mechanical properties (bending strength of *ca.* 64 MPa and tensile strength of *ca.* 36 MPa) are in the typical range for plastics and conventional wood-fibre/plastic composites, and are superior to classical wood composites such as fibreboards and particleboards. Furthermore, the outstandingly high internal bond (*ca.* 3.0 MPa) highlights the totally different adhesion mechanism operating in this new type of composite. This mechanism overcomes the common interface problems, derived from the poor adhesion between the hydrophobic matrix and the hydrophilic filler, associated with conventional wood-fibre/plastic composites. Although they are much more resistant to decay than the original unmodified wood, the obtained products seem to remain ultimately biodegradable plastic-like composites.

The same modification carried out as a surface treatment of solid wood revealed the possibility of obtaining a thin self-coating and protecting film as a result of chemical thermoplasticisation and subsequent hot-pressing. Smooth and glossy, aesthetically appealing and weathering resistant wood surfaces were obtained.

### **INTRODUCTION**

Due to its qualities, wood has been for centuries one of the most widely used materials. Its outstanding properties are due to its complex composite structure, beginning from the basic chemical composition and continuing with the cell wall structure and the anatomical structure. Wood is in fact the oldest composite material used by man.

Wood is at the same time a valuable raw material for different types of wood-based composites including mouldable products based on thermoplastic polymers and wood fillers, known as wood-fibre/plastic composites (WFPC).

The chemical composition of wood plays an important role in determining wood properties, including both its qualities and less desired characteristics, such as hygroscopicity, dimensional instability and biodegradability. Consequently, wood properties may be engineered by adequate chemical modification processes involving chemical reactions between the reactive hydroxyl groups in wood and different reagents (Rowell 1991, Militz 1997). Research around the world, especially in the last 20 years, has demonstrated the potential of chemical modification of wood. This may be designed to improve some of wood properties, such as reducing its hygroscopicity and dimensional instability and increasing wood resistance to biological attack, or to confer new properties to wood. It is well known, for instance, that wood has a limited thermoplasticity. Although it can be bent under steam and chemical treatment, it normally burns before it melts or becomes sufficiently plastic for thermally forming processes such as compression moulding, injection or extrusion. These techniques are important ways of shaping materials in rapid composites production. If wood fibres could be modified so that they become thermoplastic, then this would open up new end-uses and markets.

In this context, thermoplasticisation of wood through chemical modification, first reported by Funakoshi *et al.* (1979) and Shiraishi *et al.* (1979), seems to be a research area worthy of further development and could result in many interesting applications. A range of fibre reinforced plastics, that can be thermally formed, are available. However, these products demand a high plastic content (matrix) and a consequent low content of wood fibre. Thermoplasticisation could enable the manufacture of wood-fibre plastic composites (WFPC) through a totally different technology: the chemical modification of wood and its subsequent thermal forming. This approach would avoid the incompatibility problem between the hydrophilic wood fibres and the hydrophobic polymeric matrix used in the manufacture of mouldable WFPC by the melt-blend process. Currently, most compatibilisation methods aim to improve the compatibility of wooden filler with the polymeric matrix, whilst at the same time improving the mechanical properties and the water resistance of the resultant composites (Maldas and Kokta 1993, Oksman 1996).

Furthermore, alternative wood gluing, coating and preservation technologies may be imagined by surface thermoplasticisation of solid wood or veneers followed by hot-pressing under adequate conditions of pressure and temperature to promote a partial melting phenomenon on the surface of treated samples.

Thermoplasticisation of wood as a result of its chemical modification was explained as an *internal plasticisation phenomenon* (Shiraishi 1991) or as a consequence of an *increased free volume* resulting inside the cell wall by introducing large substituents linked to the wood matrix (Norimoto 1996). Kiguchi (1996) proposed a graphical illustration of this mechanism of chemical thermoplasticisation of wood. One interesting way of achieving wood thermoplasticisation is the esterification with dicarboxylic anhydrides followed by oligoesterification with epoxides (Matsuda 1987, Matsuda *et al.* 1988a, 1988b, Matsuda 1996).

This paper presents some research results into the thermoplasticisation of Aspen wood as sawdust, veneers or solid wood through esterification with maleic anhydride (MA) and subsequent oligoesterification with an epoxide and the further thermal forming of the chemically modified wood by hot-pressing. The properties of resulting composites are also presented.

## EXPERIMENTAL METHODS

### A Chemical modification of sawdust

Aspen wood (*Populus tremula*) sawdust was chemically modified through a two-step procedure consisting of esterification with maleic anhydride (MA) followed by oligoesterification with MA and glycidyl methacrylate (GMA), with the principal chemical equations shown in Fig. 1.

This chemical modification was carried out using a simple immersion-thermal treatment technique. Triethanolamine (TEA) was used as catalyst and N,N-Dimethylformamide (DMF) was used as solvent and wood swelling reaction medium. The oven dried unmodified sawdust (0.3-0.5 mm in diameter) was introduced into a sachet made of solvent resistant plastic mesh (0.25 mm) and impregnated with the esterification reaction mixture by immersion. The sachet was then wrapped in aluminium foil and maintained in an air-circulating oven at 120°C for 1 hour to induce the chemical reaction. This procedure was repeated for the oligoesterification step using an appropriate reaction mixture and a heating period of 6 hours at 90-95°C.

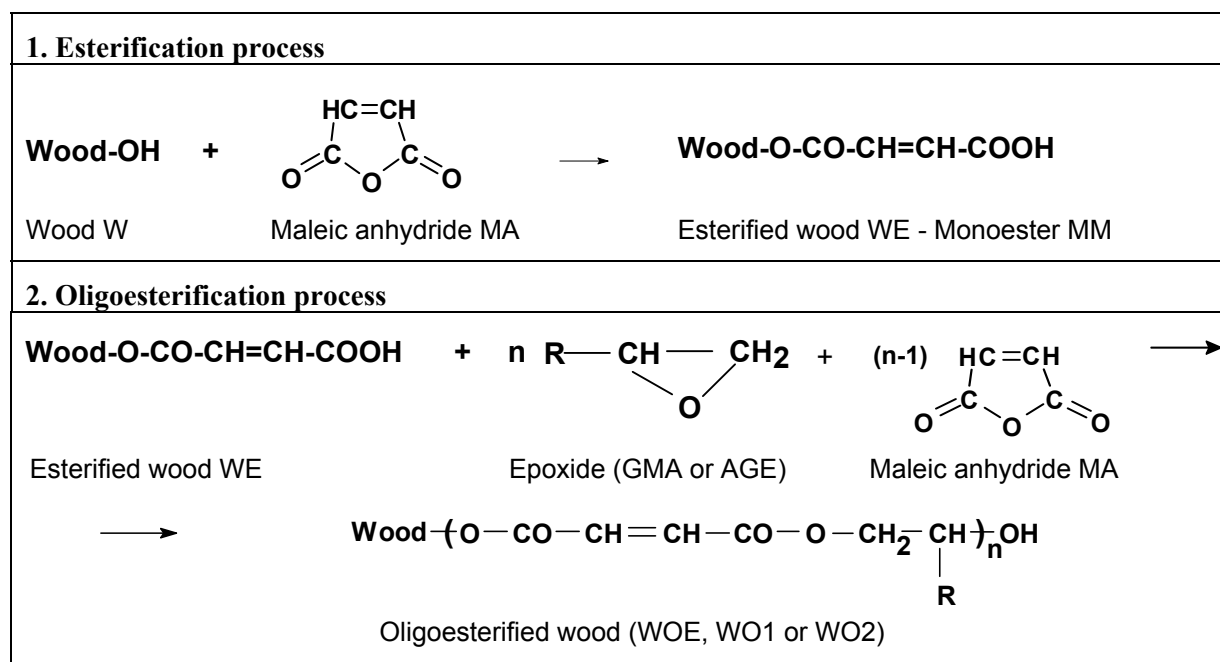


Fig. 1: Chemical modification procedure employed for thermoplasticisation of wood

A similar degree of chemical modification in the oligoesterification step was obtained by microwave heating for only one hour at 90-95°C. A microwave digestion unit (Milestone MLS-1200 Mega; from Chalmers University, Gothenburg) was used to deliver non-pulsed 250 W microwaves.

### B Chemical modification of veneers and solid wood

Aspen veneers (30 x 30 x 2 mm) and solid wood samples with radial faces (80x50x5) mm were dried at 103 ± 2°C to constant weight, prior to chemical modification. Chemical modification was achieved through a similar immersion-thermal treatment procedure as described above, except for the fact that two types of epoxy compounds were used: GMA and allyl-glycidyl-ether (AGE). The reaction conditions employed for the chemical modification of sawdust, veneers and solid wood are summarised in Table 1. After reaction, all the samples were washed carefully with acetone to remove unreacted chemicals, dried under vacuum at 20°C and then oven dried at 103 ± 2°C to constant weight. An approximate weight percent gain (WPG<sub>a</sub>), directly correlated

to the degree of chemical modification, was calculated for the modified solid wood and veneers according to Eq. (1).

$$WPG_a = \frac{M_{ra} - M_0}{M_0} \cdot 100 \quad [\%] \quad (1)$$

where:

$M_{ra}$  - represents the weight of the chemically modified sample after washing with acetone and oven drying to constant weight;

$M_0$  - represents the weight of the oven dried, unmodified sample

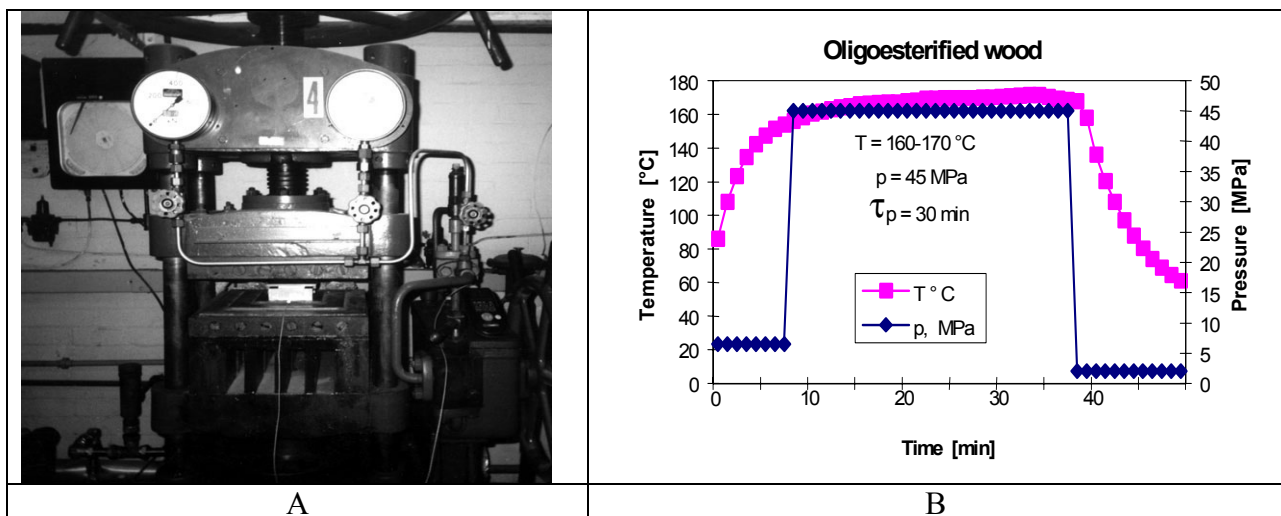
**Table 1: Chemical modification procedure for Aspen samples**

Form of wood material	Esterification			Oligoesterification			Code of sample
	Reagents	T [°C]	Time [h]	Reagents	T [°C]	Time [h]	
Sawdust	MA 29.0 %	120	1	MA 18.4 %	90-95	6	WOE
	TEA 1.3 %			GMA 35.1 %			
	DMF 69.7 %			DMF 46.5 %			
Veneers Solid wood	MA 32.0 %	120	1.5	-	-	-	WE
	TEA 1.0 %						
	DMF 67.0 %						
	MA 32.0 %	120	1.5	MA 17.4 %	120	1.5	WO1
	TEA 1.0 %			AGE 18.8 %			
	DMF 67.0 %			DMF 63.8 %			
MA 32.0 %	120	1.5	MA 12.0 %	120	1.5	WO2	
TEA 1.0 %			GMA 24.5 %				
DMF 67.0 %			DMF 63.5 %				

Note: MA – maleic anhydride; GMA – glycidyl methacrylate; AGE – allyl glycidyl ether  
DMF (N,N-Dimethylformamide) was used as a solvent in the two steps of chemical modification  
TEA (triethanolamine) was employed as a catalyst in the esterification step

**C Thermal forming of chemically modified wood**

The modified sawdust was thermally formed by compression moulding at 160-170°C and 45 MPa for 30 min to produce plastic-like boards measuring 50 mm × 60 mm × 2 mm. A rectangular mould made of hard aluminium alloy and a hydraulic 50 tonne force press (Bradeley & Turton), from Dynochem UK LTD (Duxford, Cambridge) were used (Fig. 2).



**Fig. 2: Attainment of plastic-like boards by compression moulding of thermoplasticised sawdust: A-pressing equipment; B-an example of the pressing diagram**

The veneer and solid wood specimens were thermally formed by hot-pressing perpendicular to their faces in order to evaluate if a self-protecting thin layer may be obtained on the surface of thermoplasticised wood samples, as a result of a surface partial melting process. For this purpose, half of the unmodified and chemically modified veneer and solid wood samples (coded P) were placed between polished metal plates and hot-pressed for 30 min at 130°C and 10 MPa for veneers and at 150°C and 4 MPa for solid wood, employing the same press. This procedure also made it possible to evaluate the effect of the hot-pressing on the biological resistance of the wood.

#### ***D Characterisation of the resulting products***

The structure of the resultant products was studied by Scanning Electron Microscopy (SEM). The water resistance was assessed through a repeated total immersion test in which the oven dried samples were immersed in water for 48 hours at 20 °C, oven dried and then immersed in water again for a further 48 hours. The swelling coefficients  $\beta$  [%], the water absorption values WA [%] were calculated after each immersion based on the anhydrous state prior to the respective test. The tensile and flexural properties of the composite products resulted from the compression moulding of thermoplasticised sawdust were determined according to the standardised methods for plastics (BS 2782). A method based on the principle of testing wood composites, such as chipboard and MDF, was adopted for determination of their internal bond value (IB). All the specimens were conditioned in a controlled environment room to 20 °C and 65 % RH until the equilibrium moisture content (EMC) was reached (usually for 7 days), and were tested under the same conditions. All the mechanical tests were carried out using an Instron universal testing machine (model 4311). Moreover, dielectric measurements were performed using an original method (Timar, in press). The influence of the chemical modification procedure and further thermal forming process on the biological resistance of Aspen wood products was assessed through two different tests: a laboratory decay test and a weathering test. The resistance to the wood destroying *Basidiomycetes* was determined according to a method adapted from EN 113 and ASTM D 2017-81, employing the white rot fungus *Coriolus versicolor* (Linnaeus) Quelet. After sterilisation with  $\gamma$ -radiation, the samples were subjected to attack by this fungus in pure culture for 12 weeks and the percentage weight loss caused by fungal attack (WL) was calculated.

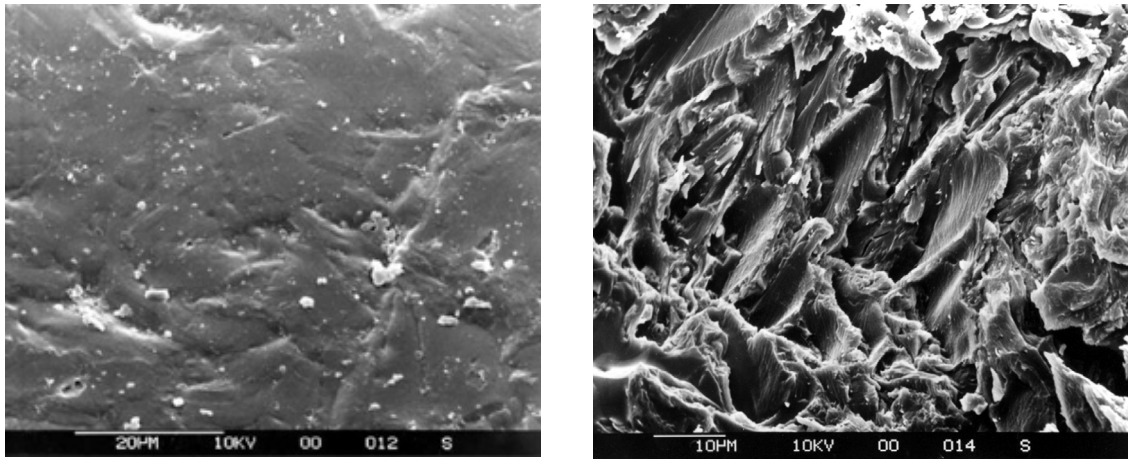
For the weathering test, modified solid wood and corresponding control samples (unpressed and hot-pressed) were exposed between July-November 1996 at Braşov-Romania. These samples were supported 2 m from the ground at 45° facing south-west. The supporting frames were constructed so that the samples would be exposed to maximum amount of sunlight and rain. Exposed samples were periodically examined visually and microscopically to determine colour and surface finish changes and extent of biological degradation.

## **RESULTS AND DISCUSSION**

#### ***A Composites resulting from the compression moulding of thermoplasticised sawdust***

Brown, plastic-like, boards with smooth and glossy surfaces resulted from compression moulding of the thermoplasticised Aspen sawdust. Although some translucent to transparent areas were present on certain samples, they were mostly opaque. The macroscopic appearance of these products was well explained by their SEM study. The photograph in Fig. 3A presents a surface aspect where the melting of the modified wood during the hot pressing is obvious. The quite homogeneous melted material is a reason for the smooth, glossy and plastic-like aspect.





**Fig. 3: SEM micrographs of the plastic-like products: A- surface aspect; B- details of the composite structure revealed in the cross-section: quasi-fibrous elements of the wood structure and melted material**

**Table 2: Physical and mechanical properties of the resultant composites (PCMWC)**

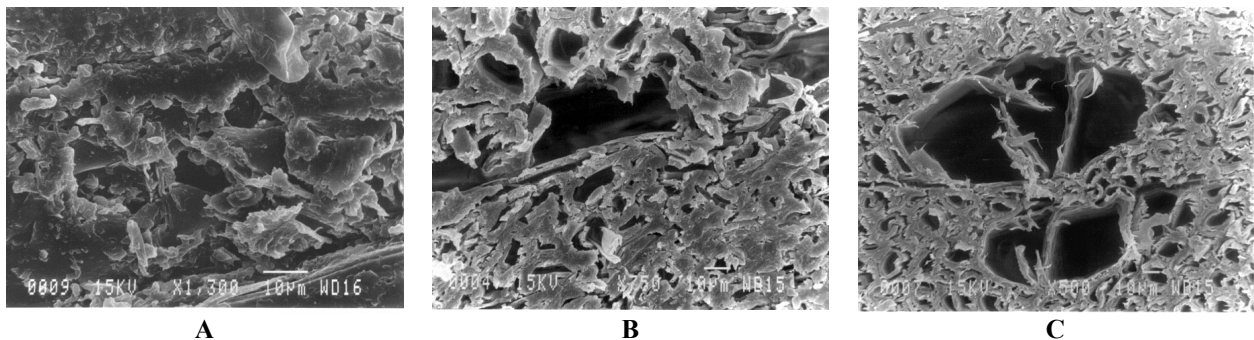
Characteristics	Experimental results			Comparative data		
	Mean	St. dev.	NS	MDF <sup>1</sup> (MR)	Chip-board <sup>2</sup>	PMMA <sup>3</sup>
<b>Physical properties</b>						
Thickness [mm]	1.898	0.087	12	Variable	variable	
Density [g/cm <sup>3</sup> ]	1.337	0.044	12	0.730-0.800	0.650-0.750	1.190
Water resistance (48 h immersion)						
<u>Test 1</u>						
Thickness swelling, $\beta$ [%]	4.17	0.47	12	5-8 (V313)	4-7 (1 h)	-
Water absorption, WA [%]	7.21	1.29	12	-	-	0.2
<u>Test 2</u>				No data	No data	No data
Thickness swelling, $\beta$ [%]	2.63	0.28	12			
Water absorption, WA [%]	5.34	1.34	12			
Dielectric properties (20°C /159 kHz)				No data	No data	(1MHz)
Dielectric constant $\epsilon$	3.2-4.05	-	6			2.8
Power loss factor $\text{tg } \delta$	0.017-0.035	-	6			0.0300
<b>Mechanical properties</b>						
<u>Flexural properties (3 point bending)</u>						
MOR [MPa]	64.07	4.22	12	40-60	15-25	72.4-131
MOE [MPa]	1886.75	168.56	12	3500-5000	2000-4000	2240-3170
MOE/MOR	29.45	-	-	83.0-87.5	133-160	24.2-30.94
<u>Tensile properties (in plane)</u>						
Tensile strength $\sigma_t$ [MPa]	35.85	4.84	18	No data	7-10	48-72.4
MOE [MPa]	1247.20	70.9	6		-	2240-3240
MOE/ $\sigma_t$	34.8	-	-			44.75-46.6
<u>Internal bond</u>						Not applicable
IB [MPa]	3.09	1.11	8	1.1-1.3	0.5-1.0	

MOR – modulus of rupture; MOE – modulus of elasticity; MDF – medium density fibreboard; MR – moisture resistant; PMMA – polymethylmethacrylat, NS - the number of samples considered in the calculation of mean value and of standard deviation (St. dev); Comparative data were taken from the following references: Caberboard Ltd Technical Guidelines (1); Walker 1993 (2); Harper 1996 (3). V313 represents a three cycle wetting test, each cycle consisting of 72 h immersion at 20°C followed by maintaining 24 h at -12°C and 72 h drying in an oven at 70°C.

Although some holes resulting from the empty spaces between adjacent sawdust particles were present, no clear evidence of the wood structure could be found on the surface. Examination of cross-sections clearly revealed a composite structure for these products. Thus, fibrous areas where cell walls and lumens, although receded, can be still easily distinguished are present

together with homogeneous areas representing the melted material (Fig. 3B). In other words, a kind of wood/thermoplastic-wood composite has been obtained. The novelty resides in the fact that this composite structure did not result by adding wood fibres or particles as fillers to a plastic cohesive matrix, rather the composite structure was the result of the partial melting of the thermoplasticised wood. The melted part of the modified wood plays the role of the cohesive matrix, whilst the unmelted wood remains as a fibrous reinforcing material. This composite structure combines the homogeneity and water resistance of plastics with the reinforcing properties of the fibrous structure of wood. The benefits of this type of structure were highlighted by the physical and mechanical properties of these plastic-like chemically modified wood composites (PCMWC) presented in Table 2. These experimental results indicate the obtained products to be high performance wood-based composites in terms of both water resistance and mechanical properties. Thus, their properties are generally superior to those of wood-based composites such as chipboard and fibreboard. What was really outstanding about the PCMWC, was their internal bond. The mean value (3.09 MPa) was at least three times higher than for the conventionally glued wood composites such as fibreboard and chipboard (0.5-1.0 MPa). Moreover, the measured value represents failures which occurred mostly (*ca.*67 % from the failure area) in the glueline between the product and the holding metal plate, meaning that the true value could be even higher than that observed. The unmelted material with a fibrous structure acts as a reinforcing material of the melted chemically modified wood and all the typical matrix/filler interface problems common to classical wood-fibre/plastic composites are overcome by this mechanism. The dielectric constant values determined for the resulted plastic-like composites (3.2-4.05) were similar to the literature values for common thermoplastics, mostly situated in the range 2 to 4 (Harper, 1996). The dielectric constant values, the power loss factor values and their variation with temperature characterised these novel composites as good insulating materials with constant dielectric properties up to about 80°C. The weight loss values after the decay test indicated that the obtained PCMWC (WL=10.94%) were far more biologically resistant than the unmodified Aspen wood (WL=76.70 %). However, the weight loss of 10.94 % registered after the test indicated that these products are still biodegradable materials.

#### ***B Composites resulting from the chemical modification and hot-pressing of solid wood***



***Fig. 4: SEM micrographs of hot-pressed thermoplasticised Aspen solid wood: surface aspect (A) and cross-section aspect near the face (B) and in the middle of the sample (C)***

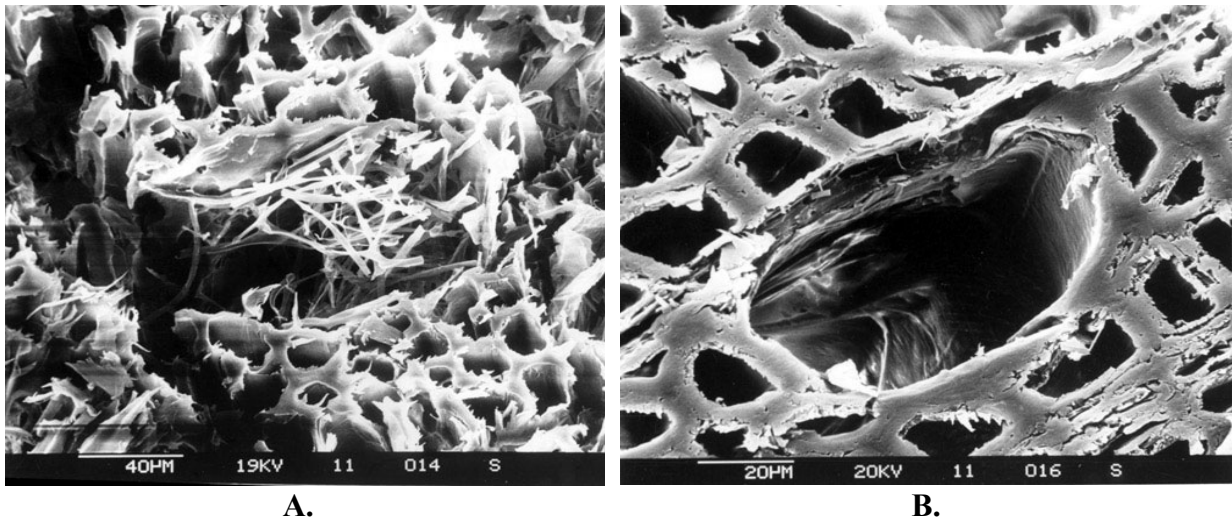
Yellowish-brown, glossy and aesthetically appealing surfaces were obtained by chemical modification followed by hot-pressing of Aspen solid wood. A microscopic investigation showed this to be due to a thin outer layer formed during hot-pressing as a result of partial melting of the oligoesterified wood with thermoplastic properties. The normal structure of wood was only little affected in the middle of the samples, so it may be considered that a multi-layered composite structure was obtained. The chemically modified wood samples showed not only an improved aspect, but also a significantly improved biological resistance in the laboratory decay test and when exposed in outdoor, above ground conditions. The results of the decay test for the chemically modified and reference veneers have been summarised in Table 3. Statistical analysis

of data referring to unpressed samples showed there were no significant differences between weight losses for the reference samples (W, C), which indicated that solvents and thermal treatment had no influence on the decay resistance of Aspen. In addition, there were no significant differences between weight losses for the chemically modified samples (WO1, WO2), although these chemical modifications significantly enhanced decay resistance of Aspen wood to *C. versicolor*. This was also revealed by a SEM study of the samples structure after the decay test (Fig. 6).

**Table 3: Percentage weight losses of Aspen veneers exposed to *Coriolus versicolor* for 12 weeks**

Type of wood	WPG <sub>a</sub> [%]	Average weight loss [%]	
		Unpressed samples	Hot-pressed samples
Unmodified wood W	0.0	61.8 (4.8)	51.8 (1.5)
Control C	0.0	51.4 (10.2)	Not determined
Oligoesterified WO1	16.0	17.8 (2.7)	15.6 (2.7)
Oligoesterified WO2	17.9	17.1 (4.3)	13.5 (1.9)

WPG<sub>a</sub> - approximate weight increase of samples due to chemical modification;  
The values in Italics between brackets represent standard deviations

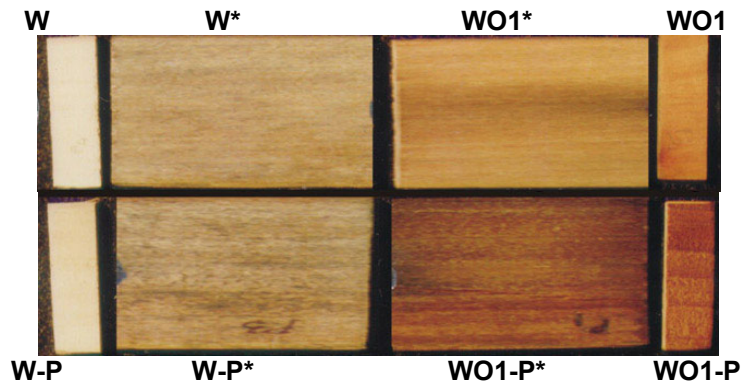


**Fig. 5: SEM micrographs of reference (control) samples (A) and chemically modified samples (B) after the decay test. Fungus hyphae colonising lumens of vessels with extensive thinning of fibre walls, as well as failures of wood structure are evident for the control samples. Little fungal colonisation or structural changes could be observed for the chemically modified wood (b)**

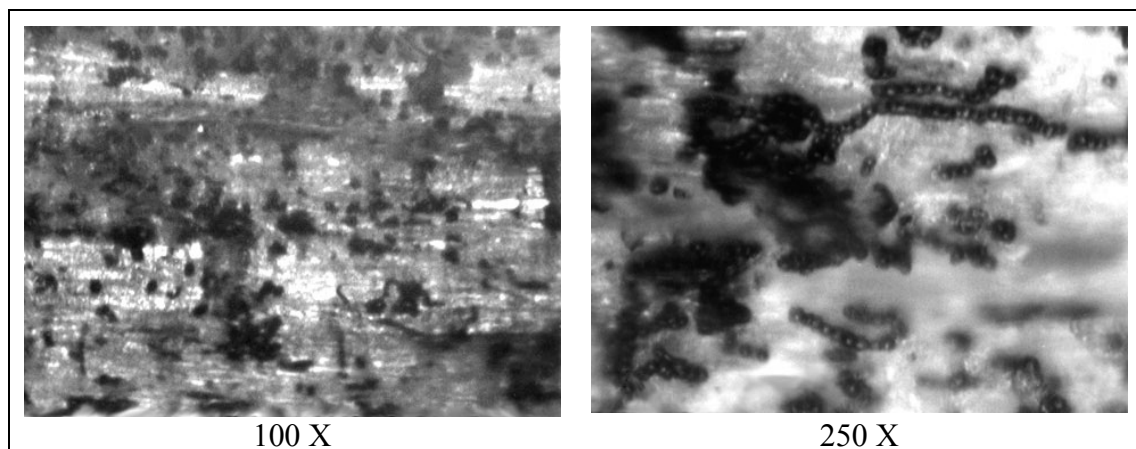
Although the average weight losses were lower for the hot-pressed veneers in all sample types, statistical analysis of the data showed these differences to be significant only for the unmodified wood specimens. This increase in decay resistance of unmodified hot-pressed veneers may be explained by compression of samples, which resulted in vessel collapse and reduced hyphal access via this cell type. Compression of the modified wood did not have such a marked effect on decay resistance and access was not the main factor influencing decay in modified specimens. Little change occurred in the aspect (colour, roughness) of the modified samples following the four-month weathering test, indicating a significant improved resistance of modified samples. In contrast, the colour of unmodified samples became grey, with a lot of black stains, and a significant roughness of the surfaces was registered. Data in Table 4 shows the results from the visual examination of samples prior to and following the weathering test. Some of these macroscopic features may be also visualised in the picture in Fig. 6.

**Table 4: Results of weathering test on Aspen solid wood**

Type of wood	Code of sample	Initial aspect	Aspect after weathering *
Unmodified	W	white, smooth, annual rings difficult to observe	colour change to grey, roughened, frequent dark stains
Unmodified hot-pressed	W-P	white, smooth, semi-glossy annual rings difficult to observe	colour change to grey, roughened, frequent dark stains
Oligoesterified	WO1	yellowish brown, annual rings clearly observed	little lightening, little change in roughness
Oligoesterified hot-pressed	WO1-P	light brown, glossy, annual rings clearly observed	little darkening, no significant changes in gloss and roughness



**Fig. 6: Comparative aspect of unmodified (W) and chemically modified (WO1) Aspen solid wood samples unpressed and hot-pressed (coded P), before (small samples) and after 6 months weathering (large samples cod\*)**



**Fig. 7: Mould fungi growing on the surface of unmodified wood samples during the weathering**

Examination of unmodified reference samples under the microscope showed biological attack had occurred during weathering (Fig. 7). The dark stains resulted from mould growth, and hot pressing before exposure and had no effect on the samples behaviour.

## CONCLUSIONS

A new type of wood-fibre/plastic composite has been obtained by a non-conventional technology. These are wood/thermoplastic-wood composites resulting from the compression moulding of thermoplasticised Aspen sawdust. These plastic-like composite products show very interesting physical, mechanical and biological properties. They are water-resistant materials and good electrical insulators. Their mechanical properties are similar to the classical wood-fibre/plastic composites and superior to wood composites such as fibreboards and chipboards.

Furthermore, the novel composites demonstrate good biological resistance to decay by white rot fungus while remaining ultimately biodegradable. The chemical modification achieved in this research not only significantly improved the decay resistance of Aspen wood, but also made possible the obtaining a thin self-coating and protecting film as a result of surface thermoplasticisation and subsequent hot-pressing of solid wood. Smooth and glossy, aesthetically appealing and weathering resistant wood surfaces were obtained.

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## Interlace Treatment – Wood Modification with N-Methylol Compounds

Andreas Krause<sup>1</sup>, Dennis Jones<sup>2</sup>, Marina van der Zee<sup>3</sup>, Holger Militz<sup>4</sup>

<sup>1</sup> Germany, Institute of wood biology and wood technology, University of Göttingen, akrause2@gwdg.de

<sup>2</sup> UK, BRE (Building Research Establishment), jonesd@bre.co.uk

<sup>3</sup> Netherlands, SHR (Stichting Hout Research), m.vanderzee@shr.nl

<sup>4</sup> Germany, Institute of wood biology and wood technology, University of Göttingen, hmilitz@gwdg.de

**Keywords:** DMDHEU, ASE, durability, N-Methylol, textile resin, cross-linking, interlace treatment

### ABSTRACT

The aim of this research project was to investigate three novel chemical products for their potential for wood modification. In order to assess suitability of these chemicals for modifying wood, the swelling and shrinking properties as well as the fixation were analysed and compared with a chemical product, which was used in previous research.

One of the greatest benefits of the two chemical products, “Arkofix NFL” and “Arkofix NEC plus”, which are based on the modified dimethyloldihydroxyethyleneurea (mDMDHEU), is that they release lower amounts of formaldehyde during the wood modification process and service life than “Arkofix NG”, which is based on dimethyloldihydroxyethyleneurea (DMDHEU). On the other hand, the DHDMI based chemical product “Arkofix NZF new” does not release any amount of formaldehyde. The effects of various catalysts, such as MgCl<sub>2</sub>, citric acid, formic acid as well as other commercial catalyst systems, Arkofix NKS and Arkofix NKD, were also investigated.

It is shown in this paper that mDMDHEU is as effective as DMDHEU in reducing the swelling and shrinking properties of wood. In addition, the wood samples treated with mDMDHEU show similar wood properties, which should be enhanced in the modified woods, as the wood samples treated with DMDHEU. MgCl<sub>2</sub> proved to be the most effective catalyst concerning the anti-shrink efficiency (ASE). However, MgCl<sub>2</sub> is hydrophilic and therefore, the treated wood samples have higher equilibrium moisture contents (EMC) when MgCl<sub>2</sub> is added in higher concentrations. Various measurements showed that citric acid is less effective than MgCl<sub>2</sub> as catalyst. Finally, the wood samples treated with “Arkofix NKS” as a catalyst showed experimental values that lie between the wood samples treated with MgCl<sub>2</sub> or with citric acid. The experimental results demonstrate that DHDMI is unable to enhance the wood properties effectively as it is almost completely leached out during the Soxhlet extraction. The results in this paper show that DHDMI cannot be used as an effective modifier for the wood.

### INTRODUCTION

It is known from some earlier researches that DMDHEU is able to enhance some wood properties (Nicholas and Williams 1987), where enhanced dimensional stability of ponderosa pine and southern pine was obtained following treatment with low concentrations of DMDHEU at elevated temperatures. Investigations in the durability of DMDHEU treated pine wood (Vidlov 1989) found approximately complete protection against the brown rot fungus

*Coniophora puteana* at higher weight gains. These results were confirmed (Militz 1993) by using different brown and white rot fungi.

A previous investigation considered the influence of concentration, temperature and catalyst on the reaction with wood with DMDHEU (van der Zee *et al.* 1998). It was shown that the dimensional stabilisation of pine wood depended upon several different factors, mainly the concentration of DMDHEU and the selected catalyst.

The textile industry has used DMDHEU since the 1960s as a cross-linking agent (Peterson 1968). A problem for the application of DMDHEU in the textile industry is the emission of formaldehyde. The same problem for the use of DMDHEU with wood could be expected. The textile industry therefore developed novel chemicals based on DMDHEU, which release a lower amount of formaldehyde, or are completely formaldehyde free. These chemicals are modified DMDHEU (mDMDHEU) or dihydroxydimethylimidazolidinone (DHDMI). These novel chemicals were used for wood modification in this research, to enhance the dimensional stability and reduce the emission of formaldehyde.

## EXPERIMENTAL METHODS

### Chemicals

All chemicals used in this project were produced by Clariant International Ltd, originally for use in the textile industry. These chemicals are usually used as cross-linking agents for an 'easy care' finishing of textiles. Treatment with DMDHEU was used as a reference in this project in comparing the efficiency of the new chemicals, which had not used before in wood modification. In addition, new catalysts and treatment methods for DMDHEU were investigated. The DMDHEU used in this research was "Arkofix NG konz" as a liquid formulation with an unknown concentration of DMDHEU. A solid concentration of approximately 70% w/w of the solution was estimated. DMDHEU can react with the two hydroxyl groups adjacent to the double bonded oxygen (see Figure 1).

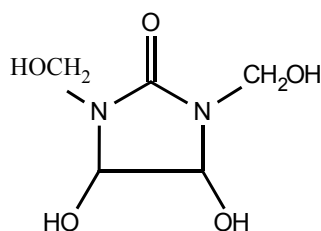
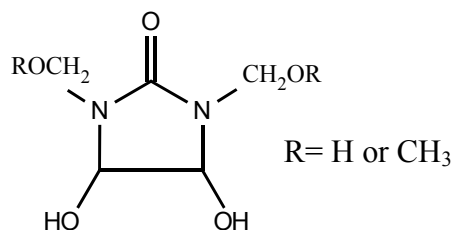


Figure 1: Chemical structure of Dimethyloldihydroxyethyleneurea (DMDHEU)

In the main reaction, these hydroxyl groups react with other reactive hydroxyl groups and form ether bonds, while water splits off.

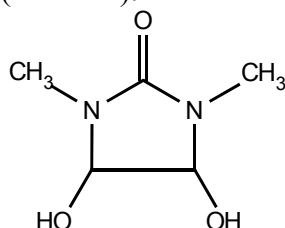
The composition of the modified DMDHEU, which is used as the chemical products in this research, was not known. In this project "Arkofix NFL" and "Arkofix NEC plus" were used, which consist mainly of modified DMDHEU. Arkofix NFL is abbreviated as mDMDHEU (a) and Arkofix NEC plus as mDMDHEU (b). DMDHEU could be modified with methanol or by adding diethyleneglycol to the ready solution (Figure 2).



**Figure 2: Chemical structure of modified DMDHEU**

“Arkofix NFL” and “Arkofix NEC plus” were available as an aqueous solution, containing an unknown concentration of mDMDHEU.

Shown in Figure 3 is another chemical used for textile finishing dihydroxydimethylimidazolidinone (DHDMI).



**Figure 3: Chemical structure of dihydroxydimethylimidazolidinone**

The main benefit of DHDMI is that formaldehyde-free finishing is possible. On the other hand, the reactivity of DHDMI with cellulose is not as good as DMDHEU. In this research “Arkofix NZF new” from Clariant Company was used.

“Arkofix NZF new” is available in an aqueous solution with an unknown proportion of DHDMI. As catalyst citric acid, formic acid, or MgCl<sub>2</sub>·6H<sub>2</sub>O was used. Additionally, two optimised catalysts were used. One of the optimised catalysts (Arkofix NKS) was used in this research for the reactions with either DMDHEU or mDMDHEU. However, DHDMI reacts with cellulose only in the presence of a special catalyst. In this project, a catalyst from Clariant (Arkofix NKD), which consists of a completely different combination of metal salt and organic acids, was used.

### **Wood**

Wood samples made from pine sapwood (*Pinus sylvestris* L.) were used. The samples were of dimensions 30 mm radial, 30 mm tangential and 15 mm longitudinal.

### **Treatment**

Three different treatment processes were investigated. The first process was the most widely used process in the textile industry and also in wood modification (Pandey 1982, Yalinkilic 1999). For this treatment, after impregnation the samples were dried at room temperature for a few days and then cured at 125°C for 16h.

The second process used the following method. (Ko 1983). After vacuum pressure impregnation as in the first process, the wood samples were reacted without drying. The wood samples were stored in a closed plastic box filled with water so that the wood blocks lay directly over the water surface. In this reaction environment, the samples were heated at 90 °C for 24 hours. After the curing stage, the samples were dried at 103°C for 24 hours.



Steam is also used in textile finishing (Cheng Chi Chen 1990). Steam at 120°C was used for the reaction of DMDHEU with cellulose. After impregnation of the wood samples as in the first process, the wood samples were put in a special reaction vessel for steam curing. In this research, pressurised steam at 100°C to 140°C was used for the reaction. Of all parameters tried, the wood samples were destroyed through the curing. Therefore, it was impossible to determine the data from this treatment. This result demonstrates that steam treatment cannot be applied effectively in DMDHEU treated wood.

### Measurements

Anti shrink efficiency (ASE) and weight percent gain (WPG) was measured and calculated as described previously (van der Zee *et al.* 1998). The wood samples were extracted for 6 hours in hot water Soxhlet extraction at approximately 90°C. After Soxhlet extraction, the changes in the weight of chemical agents that were contained in the wood samples were calculated.

## RESULTS AND DISCUSSION

### Weight change and bulking

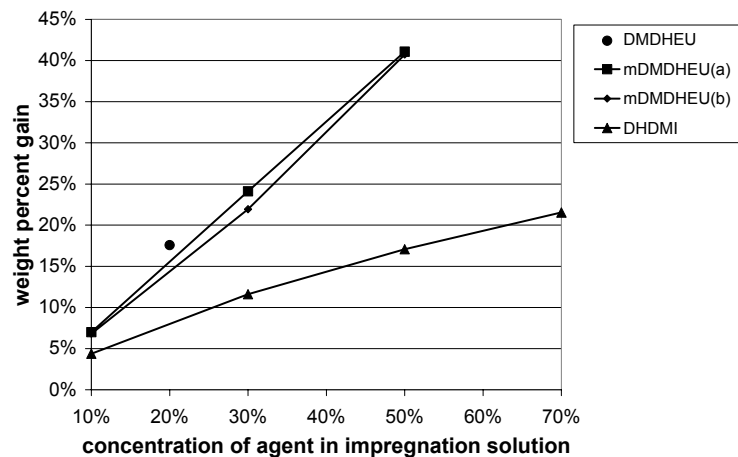


Figure 4: Weight gain of treated wood; various agents, 5%  $MgCl_2$  as catalyst

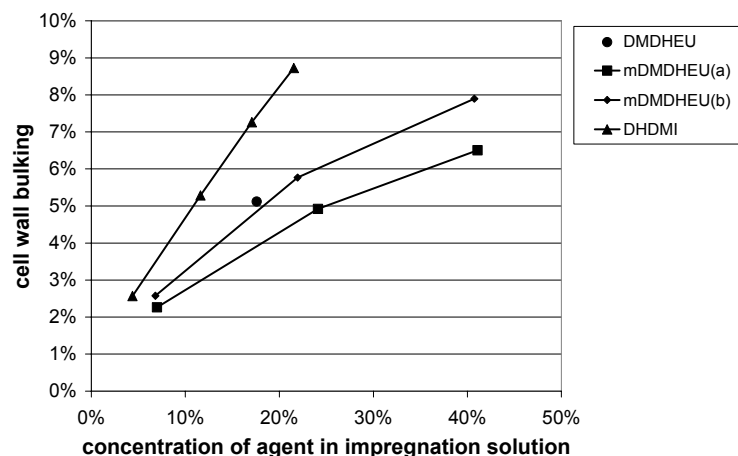


Figure 5: Cell wall bulking of treated wood; various agents, 5%  $MgCl_2$  as catalyst

An important characterisation of a new modification process is the change of the weight of wood before and after treatment. In the case of DMDHEU, weight gains were noted for each

experiment. The weight gain depended only on type and concentration of the agent used for the treatment (Figure 4). For the single chemicals, the ratio of weight percent gain (WPG) to the concentration of the agent in the bath solution was approximately the same. It can be concluded, that the agent was able to impregnate the whole wood under every concentration tested.

If a chemical is deposited in the cell wall, it becomes swollen. The agents were also able to impregnate the cell wall itself. This resulted in a cell wall bulking after impregnation and curing. For DHDMI, the ratio between the bulking percent (bp) and the WPG at all concentrations was the same. This demonstrated that DHDMI was able to easily access the cell wall. The relation between bp and WPG was not linear for the mDMDHEU. One reason for that could be that at a higher concentration, a greater proportion of the agent was not located in the cell wall but rather in the lumen.

**Equilibrium Moisture Content (EMC)**

The EMC of a wood species depends mainly on the amount of hydroxyl groups in the cell wall and the size of pores in the cell wall (Skaar 1988). The treatments in this research resulted in changed EMC. In treatments with a low concentration of agent and low concentration of catalyst, the EMC of treated wood was decreased. With increasing the concentration of agent and catalyst the EMC was also increased.

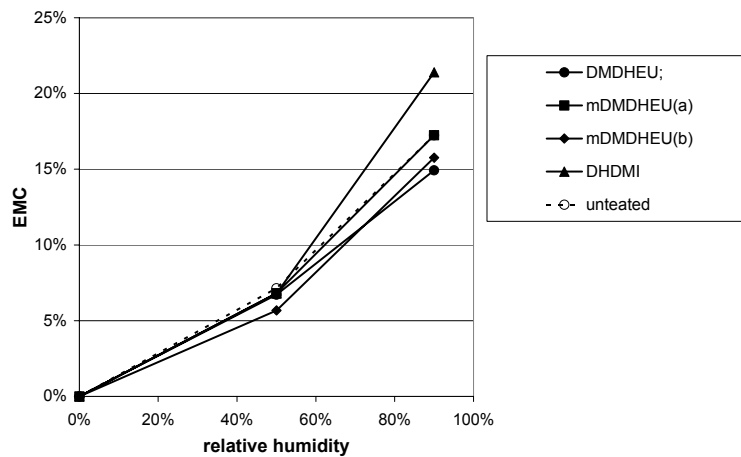


Figure 6: EMC of wood treated with various agents, 5% MgCl<sub>2</sub> as catalyst.

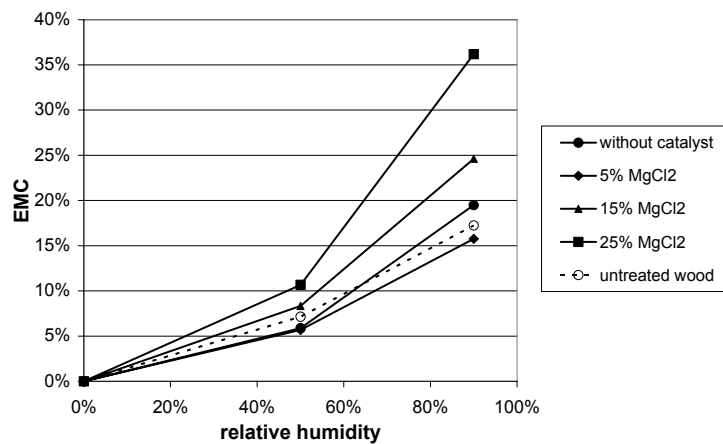


Figure 7: EMC of wood treated with mDMDHEU (a), various concentration of MgCl<sub>2</sub> as catalyst.

The EMC of treated wood samples depended on the type and concentration of catalyst (Figure 7). This showed that in wood samples treated with  $MgCl_2$  as catalyst, the moisture content increased with increasing concentration of  $MgCl_2$ .

Increasing the concentration of agent results in a higher EMC. The DMDHEU monomer has 4 hydroxyl groups. During reaction, some of these groups could co-react, or react with the wood components, with the remaining unreacted OH groups, increasing the hydrophilic character of wood (Figure 8).

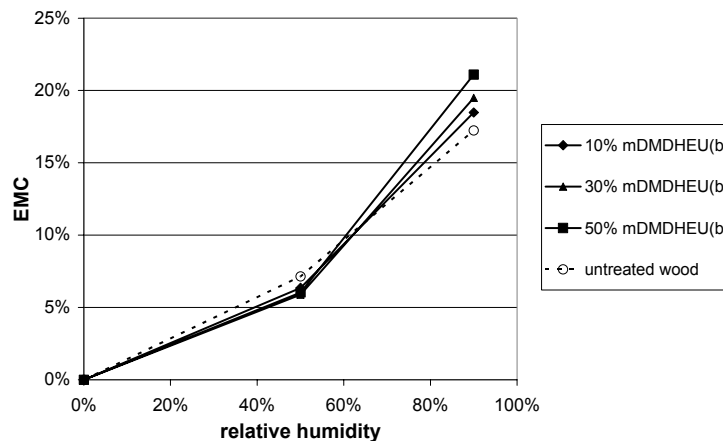


Figure 8: EMC of wood treated with mDMDHEU (b), various concentration of  $MgCl_2$  as catalyst.

### Dimensional stability

The dimensional stability was measured at 20°C between 0%, 50%, 90% relative humidity and after water saturation. The reference value for the dimensional stability is the ASE.

The ASE shows in most of the treatments very different results at changing relative humidity. With all treatment parameters, ASE values at water saturation point were increased, compared to ASE values at 90% relative humidity. ASE values improved by 50% were reached. Of basic influence on the ASE, is the type and concentration of agent (Figure 9). The results showed that with increasing the concentration, the ASE increases too. DHDMI resulted in a lower ASE at the same concentrations. This is an indication, that in this case, the efficiency of wood modification is low. This was confirmed by the results from the extraction.

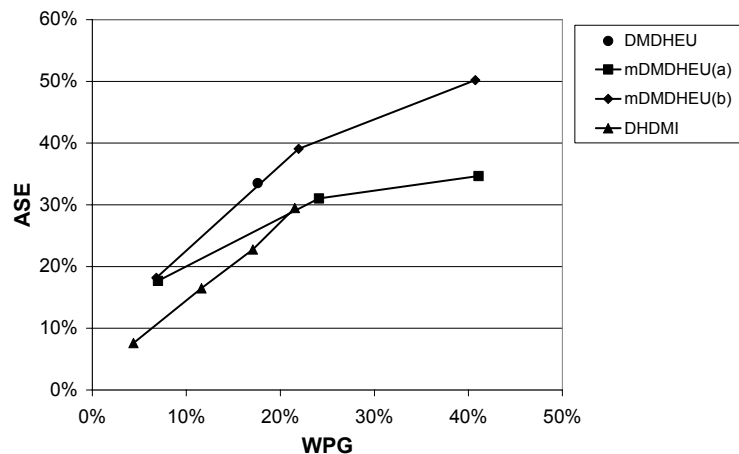
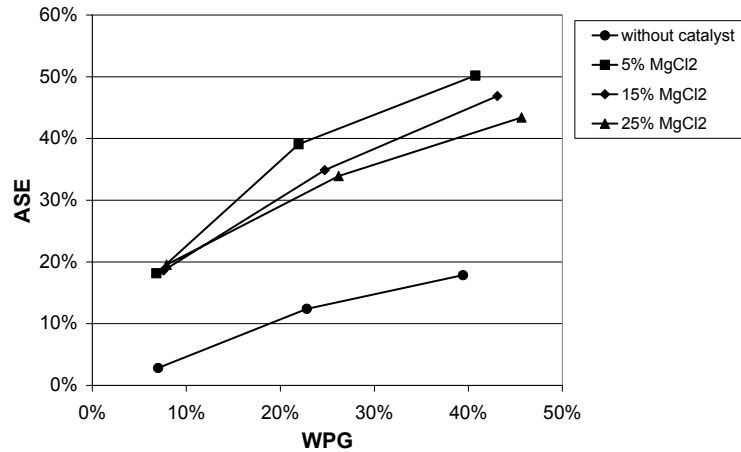


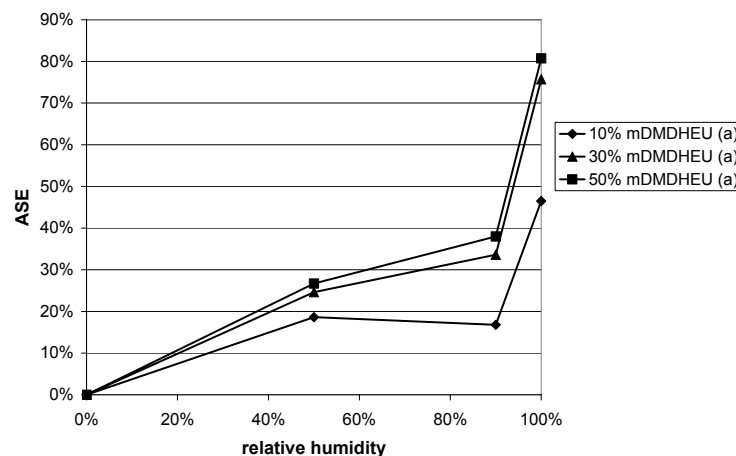
Figure 9: ASE of wood treated with various agents, 5%  $MgCl_2$  as catalyst. ASE was measured at 20°C between 0% and 90% relative humidity

Also, the type and concentration of catalyst affected the ASE (Figure 10). The reaction in the absence of a catalyst resulted in lower ASE as with the presence of  $MgCl_2$ . It could be concluded that it is necessary to use a catalyst to enhance the reaction. The concentration of catalyst has an influence on the quality of modification. With increasing the concentration of catalyst to more than 5%, the ASE decreased slightly. A reason for this could be the hydrophilicity of  $MgCl_2$ .



**Figure 10:** ASE of wood treated with mDMDHEU (a), various concentration of  $MgCl_2$  as catalyst. ASE was measured at 20°C between 0% and 90% relative humidity.

Similarly, high ASE values were measured after treatment with mDMDHEU. However, it should be noted that a different concentration range was tested for the treatment with mDMDHEU than with DMDHEU. The ASE values increased very much with increasing relative humidity from 90% to 100%. The average relative humidity in closed rooms was found to be usually in the range of 35% to 85%. It was observed that the ASE values remain relatively constant at 40% within this range of relative humidity, as can be seen in Figure 11.



**Figure 11:** ASE of wood treated with mDMDHEU (a), various concentrations of agent, 5%  $MgCl_2$  as catalyst. ASE is measured from 0% to 50% r. h., from 50% to 90% r. h. and from 90% r. h. to water saturation.

The ASE values of wood samples treated with mDMDHEU (a) were very similar to the ASE values of wood samples treated with mDMDHEU (b). This suggests that the chemical difference between these two agents is low.

Wood samples treated with  $MgCl_2$  as catalyst showed higher ASE values with the same treatments, compared with wood samples treated with citric acid as catalyst. This tendency is a common characteristic shared by all treatments with DMDHEU and mDMDHEU based modifications.

**Bulking effect and cross linking effect**

The effects of swelling and shrinking depend on uptake of water molecules by the cell wall components of wood (Skaar 1988). As water molecules penetrate into the cell wall and push the cellulose fibrils apart by inserting themselves between the hydroxyl groups of cellulose, wood becomes swollen. When the water molecules leave the cell wall later, the wood shrinks. In order to prevent this swelling and shrinking process, some effects are exploited in the wood modification. One of the effects is the bulking effect. The chemical reaction links the DMDHEU molecules to the cellulose in the cell wall. As the DMDHEU molecules are inserted between the adjacent cellulose fibres, the cellulose fibrils remain apart from each other, even when the water molecules leave the cell wall. As a result, the cell wall is held in a permanently swollen state. This effect is called the bulking effect (Figure 12).

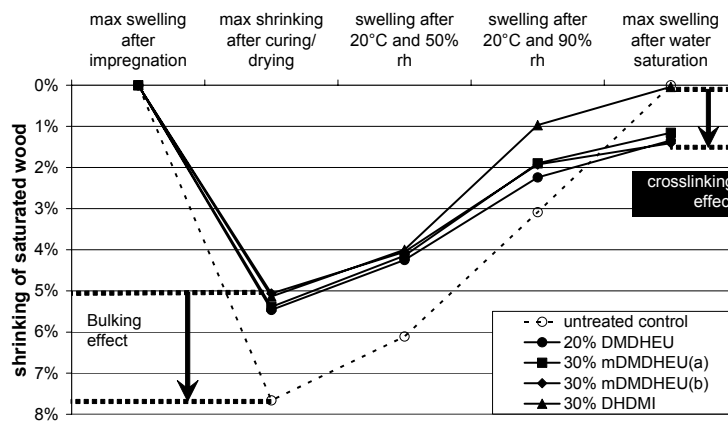


Figure 12: Tangential shrinking and swelling of wood during the treatment and measurements. Wood treated with various agents, 5%  $MgCl_2$  as catalyst.

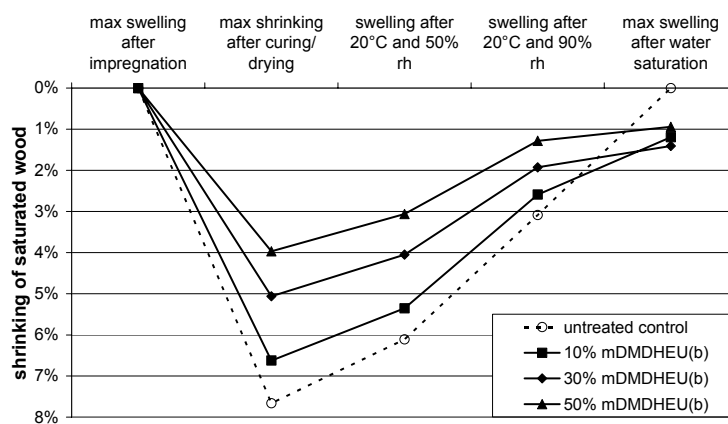


Figure 13: Tangential shrinking and swelling of wood during the treatment and measurements. Wood treated with, mDMDHEU (a), various concentrations, 5%  $MgCl_2$  as catalyst.

Another effect is that the treated wood samples after the treatment were not able to swell to the same size as after the impregnation step. This novel effect, observed for the first time in this project, is named the “cross linking effect”. The exact molecular mechanism for this effect is as

yet unclear. It is possible that the water cannot penetrate into the cell wall as well as in untreated wood. The bulking effect is observed in various kinds of treatment. On the other hand, the cross linking effect is not present in all treatments. For example, treatment with DHDMI does not show this cross linking effect as can be seen in Figure 12. Bulking is an effective parameter for revealing how good a chemical used for modifying the wood is for penetrating into the cell wall. On the other hand, the cross linking effect is a parameter that can effectively reflect the quality of the reaction between the chemical products and wood cell wall. The bulking effect depends very much on the concentration of DMDHEU, mDMDHEU and DHDMI in the impregnation solution. Figure 13 shows that the bulking effect depends more on the concentration of mDMDHEU than on the type of catalyst.

In contrast, the cross linking effect depends on the type of chemical and the catalyst as well as on the concentration of catalyst. The effect of cross linking is such a complex process that it could not be investigated further in this research.

### Leaching

When wood products are used outdoors, they are susceptible to leaching by water. Therefore, it is very important that the chemical agents remain stable in wood, even under extreme environmental conditions. A strong fixation of chemicals in the wood is necessary to prevent leaching. The fixation of DMDHEU, mDMDHEU and DHDMI was one of the parameters used to determine the effectiveness of wood modification against leaching.

The fixation of DMDHEU, mDMDHEU and DHDMI is very diverse. A very low fixation of DHDMI was measured. DHDMI leached out after every treatment process by more than 60%. These negative results were induced by the poor reaction of DHDMI with wood components (Figure 14).

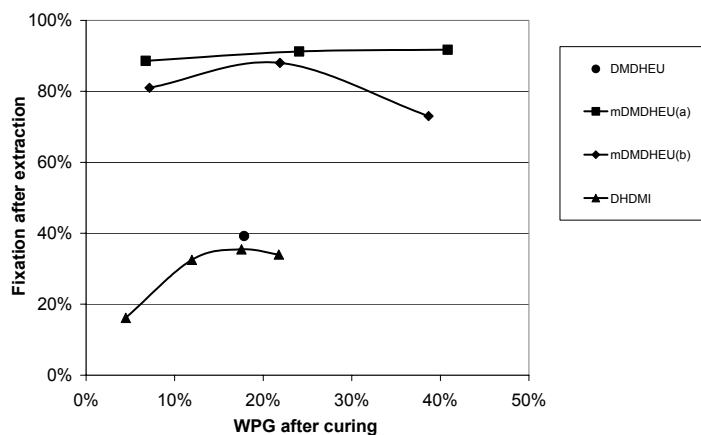


Figure 14: Fixation of agent in wood after treatment and extraction. Wood treated with various agents, various concentrations, 5%  $MgCl_2$  as catalyst.

In search for the possible reasons for the mass loss in the treated wood samples, the type and concentration of catalysts used for the treatment were compared against the mass loss of the chemical products after Soxhlet extraction. This result reveals that there might be a correlation between the mass loss and the type and concentration of catalysts. For example, wood samples treated with citric acid as catalyst and in the absence of catalyst result in one of the highest leaching rates. The higher concentration of citric acid results in the lower leaching rate. The best result was obtained from the treatment with  $MgCl_2$  as catalyst. For instance, one of the lowest mass losses was observed in the treatment with 5%  $MgCl_2$  as catalyst.

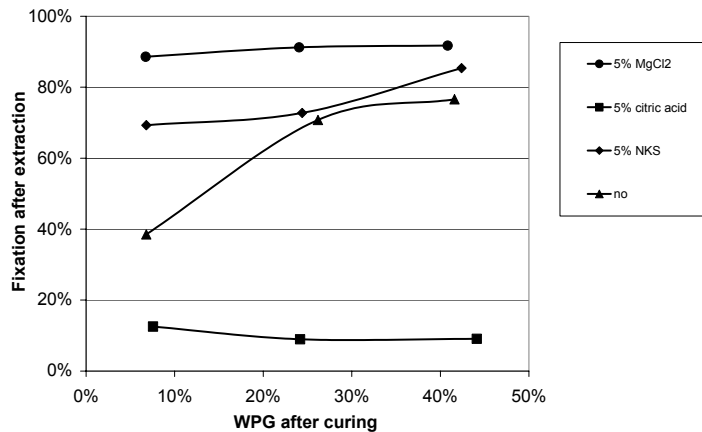


Figure 15: Fixation of agent in wood after treatment and extraction. Wood treated with mDMDHEU (b), various concentrations, various catalyst.

### FTIR Analysis

An analysis by FTIR should give more details about the nature of reaction. It is very difficult to find a good analysis method because DMDHEU, mDMDHEU and DHDMI are chemically similar to the wood components. In the textile industry, FTIR is used to analyse the reaction between DMDHEU and cotton. The double bonded oxygen in DMDHEU, mDMDHEU and DHDMI shows a characteristic peak at approximately  $1700\text{cm}^{-1}$ . This peak is changed through reaction of DMDHEU with cellulose (Peterson 1967). Therefore, by observing the change in the  $1700\text{cm}^{-1}$  peak, it should be possible to determine if the reaction took place or not.

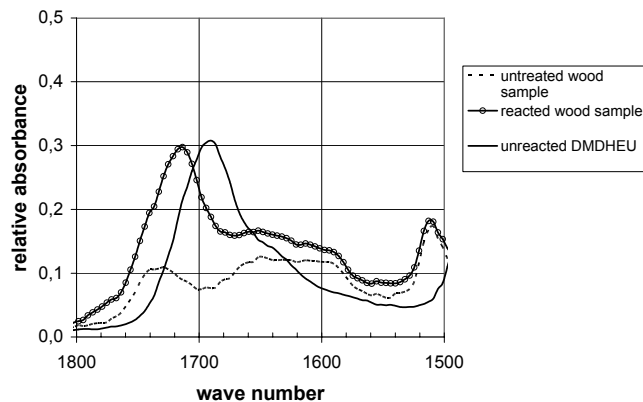


Figure 16: IR spectrum showing behaviour of the peak at  $1700\text{cm}^{-1}$ . It can be observed that the peak shifts from  $1680\text{cm}^{-1}$  to  $1720\text{cm}^{-1}$

The peak shift from  $1680^{-1}$  to  $1720^{-1}$  was caused by a change in the chemical environment surrounding of the double bonded oxygen in the DMDHEU-molecule. This was an indication that the DMDHEU-molecules bonded to the wood components.

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## Scaling Up of Some New Chemical Modification Systems

Joris Van Acker<sup>1</sup>, Antti Nurmi<sup>2</sup>, Jeremy Tomkinson<sup>3</sup>, Bauke Van der Werf<sup>4</sup>,  
Marina Van der Zee<sup>5</sup>, Mats Westin<sup>6</sup>

<sup>1</sup> Ghent University, Laboratory of Wood Technology, Coupure links 653, 9000 Ghent, Belgium. E-mail address: joris.vanacker@rug.ac.be

<sup>2</sup> VTT Building and Transport, P.O. Box 1806, FIN-02044 VTT, Espoo, Finland

E-mail address: antti.nurmi@vtt.fi<sup>3</sup> BioComposites Centre, University of Wales, Bangor, LL57 2UW, United Kingdom. E-mail address: j.tomkinson@bangor.ac.uk

<sup>4</sup> De Vries Kozijnen, Gorredijk, the Netherlands. E-mail address: bauke.vanderwerf@devrieskozijnen.nl

<sup>5</sup> SHR Timber Research, Wageningen, the Netherlands. E-mail address: m.vanderzee@shr.nl

<sup>6</sup> Swedish Institute for Wood Technology Research (Trätek), Box 5609, SE-114 86 Stockholm, Sweden. E-mail address: mats.westin@tratek.se

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### ABSTRACT

The European research project CHEMOWOOD was set up in order to support the scaling up of 5 different chemical modification systems: acrylation using N-methylolacrylamide, the MG-treatment (maleic anhydride – glycerol), succinylation, UZA-treatment (anhydride grafted linseed oil) and furfurylation. Besides a range of process improvements, the ultimate goal was to produce window frames in a scaled up process. The only exception to this was furfurylation, which was instead used for flooring and garden products.

The project considered many specific elements of scaling up. The optimisation of treating processes in relation to material characteristics was implemented in respect of specific end uses. Attempts to produce blue prints of treating plants were included, based on major concerns of efficacy over time as well as health and safety impact and environmental issues.

None of the five chemical modification systems proved to be an overall success on all criteria, especially when scaling up parameters were incorporated. Although no general outstanding system could be identified, several have potential to be used in at least niche applications. Taking into account sometimes minor disadvantages, several derived products can be considered significantly better when modified. This allows potential full implementation when process related investments are regarded as acceptable in relation to the market. In order to fully assess this potential there is still a need to balance the costs of scaled equipment investments to the volume and economics of specific commodities envisaged, as well as wood resource considered for modification. Industrial wood modification plants using some of the chemical modification systems studied are becoming however more probable now and in the near future based on trends in wood utilisation and sustainability aspects.

## INTRODUCTION

The overall objective of the CHEMOWOOD project was to develop adequate treating processes for selected chemical reactants in order to obtain wood products with enhanced properties. The best chemical wood modification system should only deal with environmentally acceptable by-products and solvents, and use simple process technology.

The milestones to reach the objective can be summarised as follows:

- Development of a process technology for selected chemical wood modification systems.
- Adjustment of the basic process in order to meet requirements of products with enhanced properties.
- Production of specific end products based on chemically modified wood and evaluation of the improved commodity properties.
- Global analysis of the ability of different treatment systems to be adopted in industrial products taking into consideration the market, the performance and the life cycle analysis.
- To design viable industrial plants for chemical modification of wood.

The CHEMOWOOD project was essentially set up to identify potential chemical modification systems for scaling up. The first criterion was to look for best options that could combine wood processing systems and chemical technology. Especially the ability to use air-dried timber and process technology developed in respect of the intrinsic wood properties were targets. Most of the work focussed on looking for simplifications in modification process parameters and solvent systems used. Based on systems combining both acceptable technology and noticeable quality improvements some commodities were produced allowing the potential introduction on industrial scale to be evaluated.

## EXPERIMENTAL

### *Chemical modification systems selected for scaling up*

Five different chemical modification systems were scaled up by each of the individual research laboratories involved in the project. At the time when this project was set up, several authors explained that next to acetylation the diversity of methods mentioned in literature was not in line with practical options for implementation on industrial scale (Militz *et al.* 1997, Westin *et al.* 1997).

The treatment with N-methylolacrylamide (NMA) is known as an easy way to graft polysaccharides with acrylic groups. In the patent literature, this acrylamide is frequently used in textile applications and in the synthesis of copolymers. In earlier research, most experiments were based on treatments using the swelling agent dimethylformamide (DMF) as solvent (Goethals and Stevens 1994). For scaling up purposes, Scots pine sapwood and beech samples were impregnated at the Ghent University with water based solutions of N-methylolacrylamide (NMA) using citric acid and aluminium trichloride as catalysts. The fact that this treatment is water-based is considered positive, as good swelling of the wood cells can still be induced this way, while no hazardous solvents are required.

A second chemical modification system was based on succinic anhydride (SA). This chemical was considered a good option selected from different anhydrides available for wood

modification, but primarily based on the simpler treating system envisaged than on the expected biological performance (Suttie *et al.* 1997). At the BioComposites Centre, based on earlier research using pyridine as solvent, a mixture of acetone and pyridine was chosen as the solvent system for succinylation. However, pyridine is toxic and is difficult to remove from wood, so when it was shown that acetone on its own was effective if heated under pressure, it was decided to dispense with it.

SHR Timber Research introduced a reactive linseed oil derivative (UZA) for scaling up. This is a modification resin based on a combination of linseed oil fatty acids and maleic anhydride. The use of a traditional oil like linseed oil with modification components was intended to combine positive elements from both.

VTT Building and Transport further developed their so-called MG system (maleic anhydride esterified glycerol) alongside several other options with maleic anhydride in different solvents. The MG modification is a water based system and has been explored also for non solid wood applications (Fujimoto *et al.* 1988). Similar to the other institutes, optimisation of curing parameters (time, temperature) for treatments with this mixture of maleic anhydride and glycerol was performed mainly by comparing the ASE (anti shrink efficiency) values of treated pine sapwood (*Pinus sylvestris*).

A last method used in the chemowood project was introduced by Chalmers University and later finalised at Trätekt. Furfurylation has a historic background (Goldstein and Dreher 1960) and is based on the use of furfuryl alcohol (FAlc) to establish different levels of PFA-loading (poly-furfuryl alcohol loading).

#### ***NMA treatments of solid wood wafers***

To give an example of some elements in the scaling up process, details are given on fundamental work related to chemical reaction and curing of the acrylation process by N-methylolacrylamide (NMA) treatment. For this initial step in the scaling up process, solid wood wafers were used.

A series of experiments with solid Scots pine sapwood (*Pinus sylvestris* L.) and beech (*Fagus sylvatica* L.) specimens was set-up to determine the optimal NMA reaction conditions, determined by WPG (=weight percent gain) and ASE (=anti shrink efficiency) data. The samples had a thickness of 5 mm in the axial direction and measured (40 x 40) mm<sup>2</sup> with the radial and tangential direction parallel to the sides.

Test parameters in a first experiment used a two step, or a one step reaction system under acidic conditions, in combination with either a 70°C, or 100°C reaction temperature:

2 steps, with step 1: 24% NMA + 1% Al(NO<sub>3</sub>)<sub>3</sub> + 1% Citric acid

and step 2: 1% K<sub>2</sub>S<sub>2</sub>O<sub>8</sub>

1 step: 24% NMA + 1% Al(NO<sub>3</sub>)<sub>3</sub> + 1% Citric acid + 1% K<sub>2</sub>S<sub>2</sub>O<sub>8</sub>

Each time, following the modification of the wood, two consecutive wetting and drying cycles were performed on the modified wood blocks by means of water impregnation, subsequent soaking at room temperature for 1-2 hours and overnight drying at 100°C. At each stage of the testing the weight of the individual blocks was recorded, as well as their tangential and radial dimensions. From these results, residual WPG and ASE values were calculated.

In a second experiment, other reaction conditions were explored. Instead of activating the OH-group of the NMA monomer to react with the OH-groups of the wood by means of the Lewis-acid system, it was suggested to activate the wood to react with the NMA under alkaline conditions. The impact of adding 2% of ammonium chloride, or 2% of zinc acetate was tested in this framework. The second option failed, while the use of ammonium chloride could also be combined with a reaction temperature of 70°C and 100°C, combined with a two step or a one step system:

- 2 steps, with step 1: 24% NMA + 2% NH<sub>4</sub>Cl  
and step 2: 1% K<sub>2</sub>S<sub>2</sub>O<sub>8</sub>
- 1 step: 24% NMA + 2% NH<sub>4</sub>Cl + 1% K<sub>2</sub>S<sub>2</sub>O<sub>8</sub>

### ***Dimensional stabilisation and biological durability***

In order to evaluate all treating systems in their scaled up version, an overall methodology protocol was established to test the material on the dimensional stabilisation and biological durability.

The test wood species beech and Scots pine sapwood were used to produce 10 replicates of square cross-section specimens with sides of 40 mm parallel to radial and tangential planes and a axial thickness of 5 mm, allowing optimal accessibility of the wood structure. For the evaluation of dimensional stability, a multiple cycle soaking-drying ageing test was used. Each cycle consists of a vacuum impregnation with distilled water, immersion overnight and subsequent drying at 103 ± 2°C for 24 hours. The anti-shrink efficiency (ASE<sub>VOL</sub>) was calculated based on comparison of modified and unmodified specimens.

Although biological durability is not a primary criterion in optimisation of process parameters for chemical modification of wood, it has always been considered an important topic in comparison to the use of biocides in traditional wood preservation. Equally, wood treated with scaled up chemical modification systems can be tested according to efficacy testing methods developed for wood preservatives like EN 113 and ENV 807. These laboratory test methods were also proven suitable when adapted for evaluation of natural durability (Van Acker *et al.* 2003) and hence considered adequate for checking biological durability of modified wood.

Wood blocks of the same wood species but in dimensions as defined by the EN 113 efficacy test against Basidiomycetes (15 mm x 25 mm x 50 mm) were uniformly treated and tested against fungal decay. The first test fungi used was *Coniophora puteana* (Schumacher ex Fries) Karsten (strain BAM Ebw. 15) for both Scots pine sapwood and beech and as second fungus *Poria placenta* (Fries) Cooke sensu J. Eriksson (strain FPRL 280) and *Coriolus versicolor* (Linnaeus) Quélet for Scots pine sapwood and beech respectively.

The assessment work on material treated under scaled up treating parameters included also soil soft rot testing, in accordance with the ENV 807 procedure.

### ***Scaling up to commodities***

In view of the use of chemically modified wood as a basic material for a range of final products, it is essential to evaluate the potential by means of pilot scale production. However, even more process adjustments are necessary and processes might not be identical for the different products. Such commodities also require testing in accordance with product evaluation systems using service testing or field tests. Although this approach exceeded the time span of the project, it was

envisaged to produce appropriate final products based on the outcome of the scaling up. The following products were envisaged to become potential applications:

- parquet flooring
- window joinery
- exterior cladding
- wet room and exterior furniture
- exterior use under soil and water contact.

## RESULTS

### *Scaling up of NMA treatments using solid wood wafers*

The results for the standard acid NMA treating system are presented in table 1. It seems that the treating schedule consisting of only 1 step results in slightly better results. The original two step system was not viable for scaling up and hence this was considered a major improvement. For the series cured at 70°C, this is also true when one takes into account that the two step reaction mechanism underwent essentially an extra leaching cycle (the second step in the treating schedule: impregnation with 1% K<sub>2</sub>S<sub>2</sub>O<sub>8</sub> in water).

*Table 1: Dimensional stability of wood wafers treated under acidic conditions with 24 % NMA solution and a curing time of 6 hours*

Wood species Treatment steps	Reaction temperature	WPG <sub>NMA</sub> (%)	Chemical stability		Dimensional stability	
			WPG <sub>D1</sub> (%)	WPG <sub>D2</sub> (%)	ASE <sub>w1</sub> (%)	ASE <sub>w2</sub> (%)
Scots pine sap / 2 steps	70°C	30.0 / 22.5	19.3	14.3	64.5	58.5
Scots pine sap / 1 step	70°C	34.7	24.9	22.3	72.2	66.4
Scots pine sap / 2 steps	100°C	32.4 / 29.6	27.8	25.5	70.5	65.4
Scots pine sap / 1 step	100°C	35.4	32.2	30.1	71.1	66.5
Beech / 2 steps	70°C	19.8 / 14.7	13.1	9.7	59.1	33.3
Beech / 1 step	70°C	18.1	13.4	11.3	48.8	31.7
Beech / 2 steps	100°C	18.7 / 16.8	15.0	13.5	46.5	39.9
Beech / 1 step	100°C	17.9	15.4	14.3	54.3	46.2

In comparison to the results of the system at 70°C, it seems that the curing temperature has no significant influence on the ASE, nor on its rate of decrease after several cyclic ageing steps. In contrast to these findings the decrease in WPG is at 100°C considerably lower.

In comparison to pine, the WPG as well as the ASE of beech are considerably lower. This can partly be explained by the lower solution uptake of beech (WPG<sub>impregnation</sub>: pine: 150% - beech: 100% resulting in a WPG<sub>NMA</sub> of approximately 1/4) as beech contains less void volume than Scots pine sapwood. For beech at 70°C, it seems that the treating schedule consisting of two steps results in better WPG and ASE values. At 100°C, the difference is however negligible. Again it can be deduced that at 100°C, the decrease in WPG after a second leaching step is considerably lower. Additionally, contrary to pine with no significant effect of temperature on the ASE, for beech the decrease in ASE is lower when reacted at 100°C.

A comparable set up as in table 1 is presented in table 2 for the alkaline treatments. The results obtained with the added acid system (table 1) are comparable to the alkaline system with NH<sub>4</sub>Cl in a one step reaction. The WPG losses again are quite high, but the ASE does not decrease proportionally. The ASE recorded for the alkaline system with NH<sub>4</sub>Cl is slightly lower than with

the acid system. Although the alkaline system could be an option, it was not considered for further development both because of this observation and the need for longer reaction/curing times. Studies of alternative reaction systems, like the ZnAc-containing treating solution, induced lower WPG- and ASE-values. Furthermore, it seemed as if all the NMA would be leached in the end as apparently no stable reaction with the wood occurred.

*Table 2: Dimensional stability of wood wafers treated under alkaline conditions with 24 % NMA solution and a curing time of 16 hours*

Wood species Treatment steps	Reaction temperature	WPG <sub>NMA</sub> (%)	Chemical stability		Dimensional stability	
			WPG <sub>D1</sub> (%)	WPG <sub>D2</sub> (%)	ASE <sub>W1</sub> (%)	ASE <sub>W2</sub> (%)
Scots pine sap / 2 steps	70°C	29.8 / 21.1	17.0	14.5	56.7	48.6
Scots pine sap / 1 step	70°C	32.2	22.9	19.7	70.3	56.7
Scots pine sap / 2 steps	100°C	30.8 / 27.3	23.0	20.1	61.1	51.5
Scots pine sap / 1 step	100°C	33.7	31.7	29.0	50.8	36.8
Beech / 2 steps	70°C	20.8 / 14.6	11.1	9.0	31.6	25.9
Beech / 1 step	70°C	20.5	13.7	9.8	54.0	30.5
Beech / 2 steps	100°C	19.9 / 17.0	13.0	10.6	35.4	24.6
Beech / 1 step	100°C	18.6	16.4	12.1	49.5	31.5

### *Dimensional stabilisation*

The dimensional stability results for the different scaled up systems in table 3 shows for Scots pine sapwood and beech, the remaining WPG (Weight Percent Gain) after the 1<sup>st</sup> (WPG<sub>D1</sub>) and 3<sup>rd</sup> (WPG<sub>D3</sub>) consecutive swelling - leaching steps. The ASE (Anti Shrink/Swelling Efficiency) is given for the third step material (ASE<sub>D3</sub>).

*Table 3: Dimensional stability of wood wafers treated with scaled up processes*

Treatment	Scots pine sapwood			Beech		
	WPG <sub>D1</sub>	WPG <sub>D3</sub>	ASE <sub>D3</sub>	WPG <sub>D1</sub>	WPG <sub>D3</sub>	ASE <sub>D3</sub>
NMA1	26	22	54	10	7	7
NMA2	24	21	53	13	11	32
SA	18	16	43	16	14	32
Acetone ref	-1	-1	2	0	0	-15
UZA1	34	33	16	12	12	2
UZA2	31	26	17	11	10	-2
MA	20	17	38	13	10	13
MG	13	10	43	9	6	14
FA11	8	7	55	16	15	48
FA12	152	152	87	79	79	91

The control acetone solvent treatment is included to elucidate the impact of pre-leaching of wood prior to modification and hence indirectly the importance of an adequate reference when assessing performance. In general, most treatments confer ASE levels of 40 to 50 % for Scots pine sapwood. Only the UZA treatments are lower at a level below 20 %. For beech, such high levels of ASE are not attainable. Next to the good results using furfuryl alcohol (FAlc), only the NMA2 (with peroxide) and the SA treatments give over 30 % ASE. The results for NMA2 using additional peroxide are better overall than for NMA1 without peroxide.

The slightly different UZA1 and 2 treatments showed no significant differences in ASE. Although the hydrophobation of the wood was very well achieved, chemical reaction seems not to be sufficient to alter the wood water relationship on a cell wall level. The swelling of UZA treated wood is hardly influenced when water is forced into the wood structure.

The comparison of maleic anhydride in alcohol (MA) with the water based MG (maleic anhydride glycerol) system pointed to a preference for the latter.

Both FA11 & 2 differ considerably in retention. The treatments retained here correspond to two different treatments levels, being 18 and 61 % WPG for Scots pine sapwood and 24 and 45 % for beech respectively for FA11 and FA12.

### **Biological durability**

Results for the Basidiomycete test in accordance with EN 113 are given in table 4.

*Table 4: Mass loss (%) of EN 113 blocks treated with scaled up processes*

Treatment	Scots pine sapwood		Beech	
	<i>Coniophora</i>	<i>Poria</i>	<i>Coniophora</i>	<i>Coriolus</i>
<b>16 weeks exposure</b>				
Control	48	43	49	48
NMA1	2	2	3	1
NMA2	2	1	3	1
SA1	26	30	13	31
SA2	24	30	16	18
UZA1	22	15	24	28
UZA2	17	14	30	21
MG1	4	2	7	4
MG2	23	19	6	8
FA11	1	3	1	5
FA12	0	0	0	0
<b>8 weeks exposure</b>				
Control	29	31	24	20
SA1	13	24	8	20
SA2	14	2	4	2
UZA1	3	4	1	6
UZA2	3	4	2	4
MG1	2	2	3	2
MG2	3	3	3	11

The percentage mass loss observed for the NMA and FA1c treatments indicate the potential for use as a wood preservative. All other modification systems altered the decay rate but, did not prevent decay. Both SA modifications (SA1 without and SA2 with 1 % NMP (1-methyl pyrrolidinone) added) were performing in a very similar but unsatisfactory way. There was even some indication that this modification system could increase decay in some circumstances. Low impact was also observed for the UZA treatments, although a slightly altered ranking of beech and Scots pine sapwood was present. This treatment clearly showed lower mass losses when intermediate results were obtained after 8 weeks testing instead of 16 weeks exposure. This can be interpreted as if the treatment is delaying decay establishment, probably linked to a hydrophobation impact. Finally, the MG treatment here presented at two slightly different retention levels is showing a typical result for non-biocidal treatments. The mechanism to increase biological durability is not based on the elimination of fungal growth but on a decrease in decay potential. Especially when looking at the results for the MG1 treatment there are no major changes in mass losses between 8 and 16 weeks exposure but still no full protection is guaranteed.

Using the criteria as mentioned in Document N34 of the European standardisation committee CEN TC 38 – Working group 23 (Fungal testing) (Van Acker *et al.* 2003) modified wood could be classified in a natural durability class (Table 5). This approach would definitely implement a



better appreciation of the MG1 treatment since the durability class 2 (durable) corresponds to the best fungal resistance observed for European wood species.

**Table 5: Durability rating scale according to Document N34 of CEN TC 38 WG 23**

Durability class	Description	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

When applications in ground contact are envisaged for modified wood, soil inhabiting organisms need to be considered and especially soft rot fungi are influencing the potential use of such treatments. Results from testing of material treated with scaled up processes, according to the European standard ENV 807, a soil soft rot test, are presented in table 6.

Most systems fail to meet the requirements of 3 or 5 % mass loss a set for wood preservatives. Only furfurylation is an adequately performing modification. Results for Scots pine sapwood might look promising but testing for only 16 weeks is not long enough to draw firm conclusions from the mass losses recorded. Based on the results for beech, none of the four other systems can be definitely recommended for in ground contact preservatives. The succinylation however proves to be far more effective against soft rot than against Basidiomycetes (Table 4).

**Table 6: Mass loss (%) of ENV 807 stakes treated with scaled up processes**

Treatment	Scots pine sapwood		Beech	
	8 weeks	16 weeks	8 weeks	16 weeks
Control	5	8	10	19
NMA1	8	12	9	7
NMA2	7	8	5	6
SA1	4	5	4	4
SA2	6	5	6	5
UZA1	13	4	14	3
UZA2	7	3	8	9
MG1	1	2	10	10
MG2	1	3	8	8
FA11	1	1	3	2
FA12	0	1	1	1

### **Scaling up to commodities**

Besides the two properties of dimensional stability and biological resistance, all scaled up treatments have been verified also for other commodity related parameters. Not only mechanical properties, but also weathering, paintability, glueability, fire resistance and ecotox were taken into account.

For the furfuryl alcohol treatment, special focus was given to the envisaged end-use parquetry and higher hazard applications like marine decking and in ground contact or water (sea water) contact end uses. The other modification systems are more applicable for window joinery and exterior cladding. For applications like exterior decking, most treatments are feasible.

In this context, furfuryl alcohol treated material has the potential to be used as a biological durable material, evaluated for flooring or equivalent applications. Surface hardness and stability are considered positive properties, while the dark colour is (especially in Scandinavia) considered an exotic aesthetic quality element. Besides a range of in ground and marine testing

carried out, several commodities were produced with furfurylated wood showing also potential in the high quality market niche.

For each of the other modification systems, a minimum of 0.07m<sup>3</sup> Scots pine timber (minimal beam dimensions of 30 mm thickness, 70 mm width and 500 mm length) was treated. At the company De Vries Kozijnen, the individual beams were planed, parallel glued with resorcinol glue, end trimmed and finger/scarf jointed to produce glulam elements as components for window frames. For this purpose, wood has been modified with the scaled up processes NMA (standard and steamed), SA, UZA and MG. Both the SA and UZA treatment were initially not successful, since delaminating of the beams could not guarantee the production of window joinery. It was deduced from this that a lower wettability or altered pH of the wood could have changed the curing of the glue. The MG treatment in the scaled up phase was not adequately performed due to a higher temperature impact causing mechanical failure when pressurised during production. The NMA treatments enabled production of window frames, but some material needed to be eliminated because of an unacceptable degree of collapse. This due to the fact that the treated beams consisted each of both sapwood and hardwood causing major differences in chemical retention within each beam and consequently non uniform drying/curing and temperature/shrinkage evolved.

Besides the technical evaluation and the process requirements, some economic features are also relevant. Topics like drying/curing requirements, solvent recovery, waste management, health and safety measures can only be fully defined when a blue-print of a treating plant is readily implemented. However, in table 7 an overview of some parameters is given that could be used to balance options for future implementation of some of these modification systems.

The positive results for the different modification systems have still to be weighed against some negative elements, like the presence of the monomer acrylamide for the NMA treatment (health and safety aspects required supervision of the chemical company Cytec) and the fact that solvents like pressurised acetone for the SA and the use of ketone for the UZA needs additional evaluation of solvent recovery systems. For the MG treatment, variable results most probably depending on only minor process differences are a disadvantage, while the high weight gain as well as the dark colour of FAlc treated wood is necessary for some applications.

*Table 7: Evaluation of scaled up chemical modification systems*

Modifier	Estimated costs of chemicals (EURO/kg)	Treating solution		Retention kg/m <sup>3</sup> or % WPG	Drying		Curing		Main positive characteristics of treatment
		Components	Solvent		time (h)	temp. (°C)	time (h)	temp. (°C)	
NMA	0.8 €	NMA 24% Al(NO <sub>3</sub> ) <sub>3</sub> 1% Citric acid 1% Peroxide	Water	25% WPG	16	40	8	100	50% ASE water-based
SA	2.0 €	SA 10%	Aceton	50 kg/m <sup>3</sup> 20% WPG	Oven dried		2	120	40% ASE
UZA	2.2 €	UZA 25%	Ketone	30% WPG	Oven dried		12	125	water repellency
MG	1.2 € for MA, 0.6 € for glycerol	MA 3 mol (15%) Glycerol 1 mol (5%)	Water	25% WPG	12 4	50 90	4	170	40 % ASE water-based
FAIc	1.0 €	FAIc: 15-92% Citric acid: 0.75-2% Cyclic carboxylic anhydr.: 0.3-1% Water: 4-5% EtOH/MeOH: 0-80%	Water Ethanol	10-120% WPG	16	20-40	12	103	50-90 % ASE

## DISCUSSION

### *Scaling up of NMA treatments using solid wood wafers*

The example of process optimisation given for the N-methylolacrylamide (NMA) treating system shows clearly the multitude of parameters already to be considered without even taking into account far higher wood quality variability than the readily accessible wood wafers of Scots pine sapwood and beech used. It remains however essential that treating solutions and process conditions do not require high investments, complicated health and safety measures, nor high running costs which are unacceptable for industrial use. The fact that beech is not equally improved by acrylation to the same extent as Scots pine sapwood, reveals that for each wood species specific treating parameters need to be optimised. When taking into account also the impregnation process variables linked to dimensions, moisture content and the sometimes refractory behaviour of wood species, there is a long way from laboratory experiments using small blocks in optimal conditions (axial accessibility, swelling solvent, oven dried material, defect free) to practical industrial conditions. For NMA treatments, this involved kiln drying, water based treating solutions with specific pH, adding special peroxides, curing at moderate temperatures and last but not least working conditions under health and safety restriction of a chemical plant using an acrylamide monomer.

### ***Dimensional stabilisation and biological durability***

When optimal laboratory conditions have been altered in acceptable scaled up conditions, there is a need to check whether the new process parameters still enhance the wood quality the same way with regard to dimensional stabilisation and biological durability. Sometimes a compromise between parameters that are impossible to balance is needed. This is even more significant when taking into account the commodities envisaged. This way it is feasible to say that no scaled up modification fails but that the number of potential end uses can become restricted.

### ***Scaling up to commodities***

Although some commodities were produced based on scaled up modification processes, most researchers involved agree that a pilot scale step is needed for industrial implementation. Such a step has been identified as being very crucial when other wood modifications systems were aiming at introduction on an industrial scale. Although it can be considered technically feasible to produce high quality products based on modified solid wood, this does not necessarily lead to success. A parameter that should not be neglected is the total volume of wood that is envisaged to be treated on an annual basis and the availability of wood resources adequately compatible to the restrictions of the modification process.

## **CONCLUSIONS**

When scaled up, none of the five chemical modification systems proved to be an overall success on all criteria. Although no general outstanding system could be identified, several have potential to be used in at least niche applications. Taking into account sometimes minor disadvantages, several derived products can be considered significantly better when modified. This allows potential full implementation when process related investments are regarded as acceptable in relation to the market. In order to fully assess this potential, there is still a need to balance the costs of scaled equipment investments to the volume and economics of specific commodities envisaged as well as wood resource considered for modification. Industrial wood modification plants using some of the chemical modification systems studied are becoming however more probable now and in the near future based on trends in wood utilisation and sustainability aspects.

## **ACKNOWLEDGEMENTS**

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## Mechanical Properties of Acetylated Solid Wood Treated on Pilot Plant Scale

H.P.M. Bongers<sup>1</sup>, E.P.J. Beckers<sup>2</sup>

<sup>1</sup> SHR Timber Research, PO Box 497, 6700 AL, Wageningen, the Netherlands, f.bongers@shr.nl

<sup>2</sup> SHR Timber Research, PO Box 497, 6700 AL, Wageningen, the Netherlands, e.beckers@shr.nl

**Keywords:** mechanical properties, acetylation, process influence, acetic acid, pilot plant scale

### ABSTRACT

Wood acetylated with different processes on pilot plant scale has been used to determine the mechanical properties of acetylated beech (*Fagus sylvatica* L.), poplar (*Populus spec.*), Scots pine (*Pinus sylvestris* L.) and radiata pine (*Pinus radiata* D. Don.). In this research, the Modulus of Elasticity (MOE), Modulus of Rupture (MOR), impact resistance, Janka hardness, shear strength, resistance to axial withdrawal of screws and compression parallel to the grain were determined. The equilibrium moisture content and density of acetylated and untreated wood were also determined, because of their influence on the mechanical properties. The effect of acetic acid, formed as a by-product during the acetylation reaction, on the mechanical properties (MOE and MOR) was investigated. The results show that the acetylation process affects almost all tested mechanical properties. In some cases, the mechanical properties were increased by acetylation, especially with Scots pine and poplar. On the other hand, MOE and MOR of radiata pine were decreased by acetylation. Almost no change in mechanical properties could be determined for acetylated beech. These “shifting” results can be explained by considering the various effects of the acetylation process on the strength properties. Negative effects on the mechanical properties are the relatively reduced fibre amount per cross section and the reduced degree of polymerisation of the acetylation medium. The lower equilibrium moisture content of acetylated wood affects the mechanical properties positively. The mechanical properties of acetylated wood are the net result of the negative and positive effects during the acetylation process. The effect of acetic acid on the mechanical properties of wood in the long term, however, are still unknown.

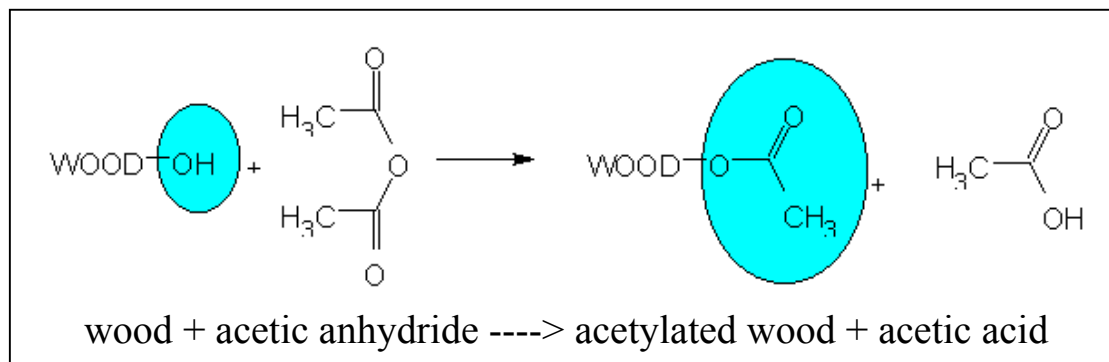
### INTRODUCTION

Acetylation with uncatalysed acetic anhydride has been studied extensively and shown to be one of the most promising methods for improvement of technical properties of wood products. During the reaction of the wood with acetic anhydride, hydroxyl groups of the cell wall polymers are converted into acetyl groups (Fig. 1).

The durability and dimensional stability of a wood species can be improved considerably by acetylation (Beckers *et al.* 1998, Beckers and Militz 1994, Beckers *et al.* 1994, Goldstein *et al.* 1961, Larsson and Simonson 1994, Larsson-Brelid *et al.* 2000, Militz 1991, Rowell *et al.*, 1989, Singh *et al.* 1992).

Since 1992, SHR Timber Research has been involved in research on acetylation of solid wood. The principle was proven initially at laboratory scale. After some years of work, a pilot plant (2500 litres with 0.6 m<sup>3</sup> wood capacity per batch) was built by Acetyleer Kennis BV (AKBV) in

1999. Since the establishment of the pilot plant, SHR has conducted several experiments and results indicate good potential for the commercial acetylation of wood.



*Figure 1: The reaction of wood with acetic anhydride*

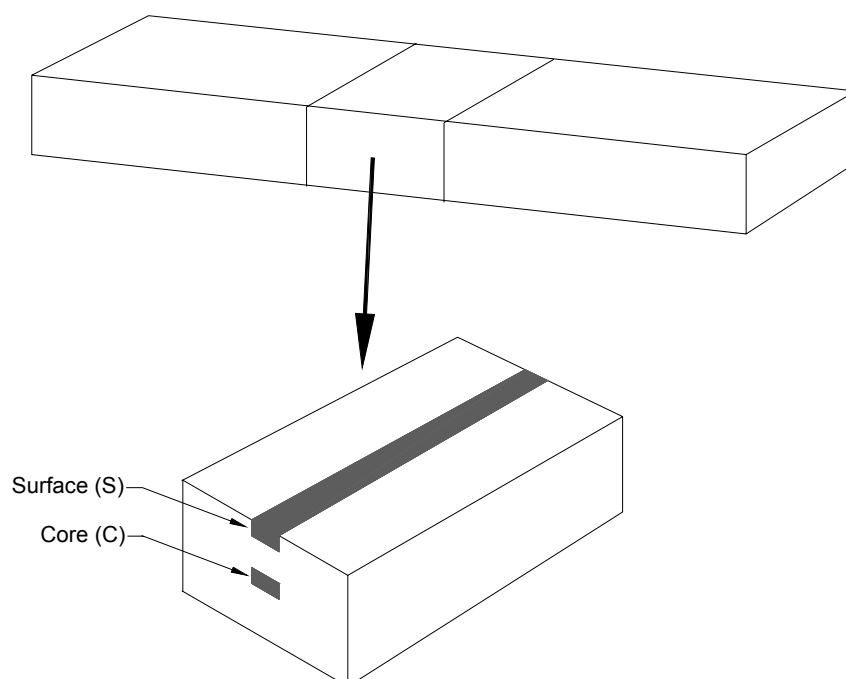
For load bearing applications, the mechanical properties of wood are very important. Tests on small samples (treated on laboratory scale) showed that mechanical properties are not considerably altered by acetylation (Akitsu *et al.* 1993, Dreher *et al.* 1964, Goldstein *et al.* 1961, Larsson and Tillmann 1989, Militz 1991). The strength properties of acetylated wood, however, seem to vary for different wood species. Dreher *et al.* (1964) and Larsson and Tillmann (1989) discuss the non-uniform results, and relate the mechanical properties of acetylated wood to increasing and decreasing effects of the acetylation process. Due to a relatively decreased amount of fibres per volume and a possible reduction of the length of the cellulose chains (due to acetic acid and warm conditions during acetylation), the mechanical properties of acetylated wood are decreased compared with untreated wood. On the other hand, the acetylation process influences the mechanical properties positively, due to the lower equilibrium moisture content.

In this research, the mechanical properties of acetylated wood on pilot plant level have been studied, in order to investigate the possible influence of up-scaling of the acetylation process on the mechanical properties. Results are also presented of the influence of acetic acid on the short term strength properties of acetylated wood. Acetic acid is formed as a by-product during the acetylation reaction (see Fig. 1). To remove this acetic acid, a post treatment is necessary. Steaming (with water) is one of the post treatments developed. During this post treatment the wood contains water and acetic acid. Combined with elevated temperatures during the post treatment (above 120°C) this could result in reduction of the mechanical properties of the wood (Niemz 1993).

## EXPERIMENTAL METHODS

### *Wood*

Commercial sized samples (up to 4 meters in length), acetylated in various pilot plant batches, were used to determine the mechanical properties of acetylated wood. The wood species used were beech (*Fagus sylvatica* L.), poplar (*Populus spec.*), Scots pine (*Pinus sylvestris* L.) and radiata pine (*Pinus radiata* D. Don). For Scots pine and radiata pine, samples were taken from batches where either the acetylation time, or post treatment differed. At least 12 clear (failure free) wood samples per category were sawn from the core (C) and surface part (S) of a board from the board's middle, for testing of the mechanical properties (Fig. 2). An overview of the "raw" material is given in Table 1, while in Table 2 the dimensions of the test samples are given.



**Figure 2:** Location of the samples from the surface (S) and core (C) of the board for testing of the mechanical properties.

**Table 1:** Overview of the “raw” wood samples

Wood species	Batch number	Wood dimensions t x w x l [mm]	Acetylation time [min]	Post treatment
Poplar	-	25 x 150 x 480	-	-
Beech	-	25 x 150 x 480	-	-
Scots pine	609	28 x 155 x 3800	195	9x steaming
	610	28 x 155 x 3800	240	steam stripping
	611	28 x 155 x 3800	330	9x steaming
	620	28 x 155 x 3800	330	9x steaming method 2
Radiata pine	617	40 x 150 x 4000	330	9x steaming
	618	40 x 150 x 4000	330	20x steaming
	619	40 x 150 x 4000	400	9x steaming

To investigate the influence of acetic acid on the strength properties of acetylated wood, 200 Scots pine (*Pinus sylvestris* L.) stakes of 20 mm x 20 mm x 350 mm and 120 Scots pine stakes of 5 mm x 10 mm x 100 mm were used in total. These stakes were divided into three groups:

- untreated
- acetylated with steaming post treatment (3 runs)
- acetylated with steaming post treatment (9 runs)

To investigate the influence of acetic acid, only a part of the untreated and acetylated with steaming as post treatment (3x), were also impregnated with three different acetic acid concentrations (3,5%, 10% and 30%).

### **Acetylation and Post Treatment**

Commercial sized timber was acetylated in the pilot plant of AKBV, according to the process schedule represented in Figure 3. The acetylation time and post treatment were varied, in order to determine their influence on the strength properties. Table 1 gives an overview of the acetylation time and post treatment per wood species and batch number.



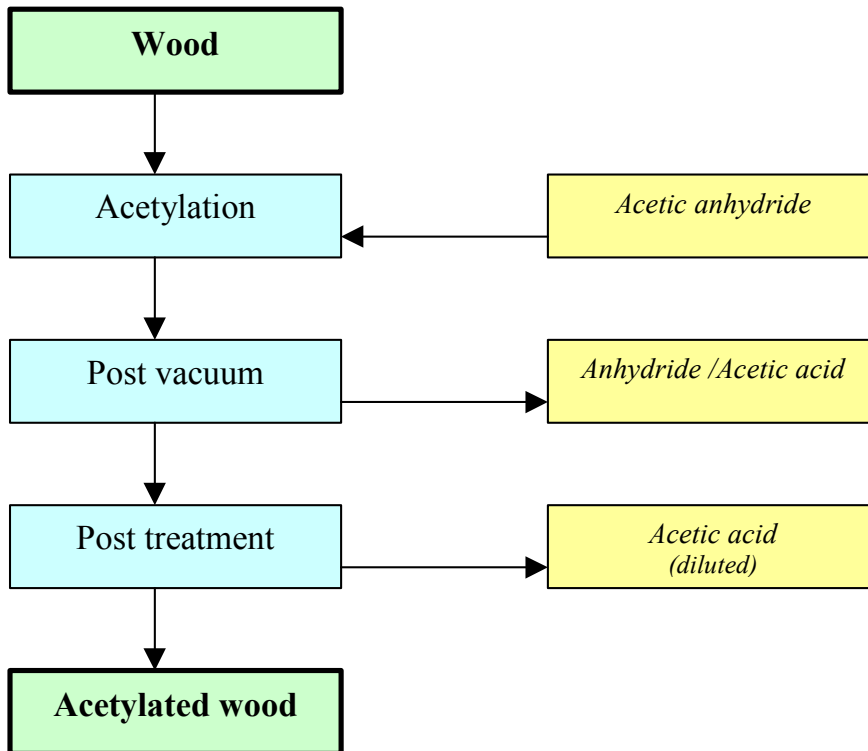


Figure 3: Steps in the acetylation process

The samples used for the investigation of the influence of acetic acid on the mechanical properties were acetylated in the pilot plant. After acetylation, samples were extracted during the post treatment after 3x steaming and after 9x steaming.

A part of the untreated and acetylated with 3x steaming as post treatment, were also impregnated with three different acetic acid concentrations (3,5%, 10% and 30%).

To investigate the influence of temperature and duration of the post treatment on the mechanical properties, all samples were finally dried in an oven to remove the acetic acid according to one of three different drying schedules:

- Slow drying: each 24 hours the temperature of the oven was increased to 40, 60, 80, 100 and finally 5 hours at 120 °C.
- Intermediate drying: approximately 90 hours at 103 °C and 5 hours at 120 °C.
- Fast drying: approximately 95 hours at 120 °C.

#### **Measurements and methods**

The acetylation level (acetyl content) of the wood samples after acetylation was determined by High Performance Liquid Chromatography (HPLC) analysis. The method consists of refining wood into woodmeal, saponification (de-acetylation) with an excess of sodium hydroxide, and quantitatively determination of the acetate amount by HPLC (Beckers *et al.*, 2002).

The amount of acetic acid after acetylation and impregnation with acetic acid was determined on refined wood samples (wood meal). The acetic acid inside the wood meal was washed out using water. After filtration, the acid value was determined by titration, and calculated for the acetic acid value (weight) of the oven-dry weight of the wood sample.

The following mechanical properties of untreated and acetylated poplar and beech samples were determined:

- Modulus of Elasticity (MOE) using a four-point bending test according to DIN 52186
- Modulus of Rupture (MOR) using a four-point bending test according to DIN 52186
- Impact resistance with a 7 J hammer where the amount of energy needed for braking the sample is registered
- Janka hardness of the radial and tangential surface by pressing a steel bullet (diameter 11,284 mm) to its centre in the wood with a speed of 5 mm per min.
- Shear strength according to a test norm relating to plywood (EN 314-1), with the exception that 20 mm x 20 mm samples were used instead of the prescribed 25 mm x 25 mm.
- Resistance to axial withdrawal of screws according to EN 1383
- Compression parallel to the grain according to DIN 52185

For untreated and acetylated Scots pine and radiata pine, only the MOE and MOR were determined by using a three-point bending test (DIN 52186). Apart from mechanical properties, the equilibrium moisture content was determined, and density of the acetylated and untreated wood at 65% relative humidity and 20 °C was calculated.

*Table 2: Overview of the dimensions of the test samples per test*

Test	Thickness [mm]	Width [mm]	Length [mm]
MOE / MOR	20	20	350
Impact resistance	10	10	150
Shear strength	20	20	100
Resistance to axial withdrawal of screws	40	40	10
Compression parallel to the grain	20	20	50

The samples to investigate the influence of acetic acid on the strength properties were conditioned at 65% relative humidity and 20°C, after drying. The MOE and MOR was determined for 10 samples per group (untreated, untreated impregnated with acetic acid, acetylated with 3x steaming, etc.), according to DIN 52186.

## RESULTS AND DISCUSSION

### *Mechanical properties of acetylated wood on pilot plant scale*

The effect of acetylation on the mechanical properties relative to the untreated wood species is summarised in Table 3. A statically significant relative change (according to the t-test) to the untreated wood is expressed as “-” or “+” for a decrease or increase respectively. No significant change in comparison to the untreated wood is expressed as “=”. The various acetylation processes for Scots pine and radiata pine (see Table 1) are indicated in Table 3, by using the batch number as description. The addition of the letter in these headings relates to the position of the sample in the “raw” material (Centre of the board (C) and Surface (S), respectively).

**Table 3: Overview of the effect of acetylation on the mechanical properties**  
 (- :decrease, = :no change + :increase)

Wood species	Beech	Poplar	Acetylated Scots pine								Acetylated radiata pine					
			609 C	609 S	610 C	610 S	611 C	611 S	620 C	620 S	617 C	617 S	618 C	618 S	619 C	619 S
Equilibrium moisture content [%]	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
Density [g/cm <sup>3</sup> ]	=	+	+	+	+	+	+	+	+	+	=	+	=	+	=	=
MOE [N/mm <sup>2</sup> ]	=	+	+	+	+	+	+	+	+	+	-	=	-	=	-	-
MOR [N/mm <sup>2</sup> ]	-	+	+	+	+	=	+	=	=	=	-	=	-	=	-	-
Compression parallel to the grain ([/mm <sup>2</sup> ])	+	+														
Janka hardness [N/mm <sup>2</sup> ]	=	+														
Shear strength [N/mm <sup>2</sup> ]	=	+														
Resistance to axial withdrawal of screws [N/mm <sup>2</sup> ]	-	=														
Impact resistance [N/mm <sup>2</sup> ]	=	=														

The results show that in some cases the mechanical properties (MOE, MOR, compression parallel to the grain, Janka hardness and shear strength) are increased by acetylation, especially with Scots pine and poplar. On the other hand, the MOE and MOR for radiata pine were decreased by acetylation. Almost no change in mechanical properties occurred after acetylation of beech. Research from Dreher *et al.* (1964) showed that the compression strength, hardness, fibre stress at proportional limit, and work to proportional limit were increased by acetylation for oak, maple and ponderosa pine. They found a decrease in bending strength for maple and oak, while the bending strength of ponderosa pine increased due to acetylation. Other research showed that the Modulus of Elasticity and Modulus of Rupture remained unchanged by acetylation, and shear strength was slightly reduced by acetylation (Akitsu *et al.* 1993, Goldstein *et al.* 1961, Larsson and Tillmann 1989, Militz, 1991). All these results show that the influence of acetylation on the mechanical properties is not always uniform.

#### ***Influence of the acetylation process***

By understanding the effect of the acetylation process on the mechanical properties, the non-uniform results of the mechanical properties can be explained. The overall mechanical properties of acetylated wood relate on varying increasing and decreasing effects resulting from the acetylation process (Dreher *et al.* 1964, Larsson and Tillmann 1989).

Increase of mechanical properties:

- The lower equilibrium moisture content of acetylated wood in comparison with untreated wood under identical circumstances. Therefore, acetylated wood should have increased mechanical properties, since mechanical properties increase with decreasing moisture content (Tsoumis 1991, Kollmann and Côté 1968).
- Density has substantial influence on the mechanical properties of untreated wood. A higher density will result in higher strength properties (Tsoumis 1991). Acetylation often increases density, however according Larsson and Tillmann (1989) this increased density of acetylated wood is not believed to influence the strength properties since the acetyl groups are mainly situated as side groups on the existing wood polymers.

Decrease of mechanical properties:

- Acetylated wood is permanently swollen. The amount of fibres and lignocellulose is therefore decreased per volume, compared to untreated wood. This reduced amount of fibres has an effect on several mechanical properties, such as the shear strength.
- The acetylation process includes heat treatment (hydro-thermal effects) under acetic conditions (caused by acetylation agent and by-product respectively), which causes a certain amount of degradation of various chains of cellulose, hemi-cellulose and lignin, resulting in a reduction of mechanical properties. Hydro-thermal effects on the strength properties have been studied intensively, since their importance for thermal modification of wood, and a negative influence of higher treatment temperature on the strength properties is observed (Kollmann and Côté 1968, Stamm 1964, Tjeerdsma *et al.* 1998, Vernois 2000). Furthermore, degradation of wood polymers can occur under acidic circumstances (Lai 1991).

When the results of the bending strength (MOR) and Modulus of Elasticity for the various acetylated radiata pine are considered, a difference between the centre (C) and the surface (S) of a 40 mm board can be observed. For batches 617 and 618, the strength properties were reduced in the centre of the board, while the strength properties remained unchanged at the surface. This difference in density is not believed to explain this result, since the acetyl groups are not within the load-bearing wood structure. A factor that could explain the difference between the strength properties of the surface and the centre of the board is the equilibrium moisture content, which depends on the acetylation level. The acetyl content, determined by HPLC, of the surface and centre of the 40 mm x 150 mm radiata pine board is mentioned in Table 4 for batches 617 and 618.

**Table 4: Acetyl content and residual acetic acid after post-treatment for batches 617 and 618**

	Batch 617		Batch 618	
	Surface	Centre	Surface	Centre
Acetyl content (determined by HPLC)	15.9	14.8	16.0	12.6
Amount of acetic acid after post-treatment [%/dry mass wood]	2.8	4.4	1.6	3.5

Although there is a small acetyl content difference between board surface and centre, it is not believed that this difference results in significant difference in strength properties of the acetylated wood. It is believed that hydro-thermal effects are more pronounced in the centre of the board, since the heat generated by the exothermal acetylation reaction is “stored” in the centre of the board. Although the same amount of heat (or more when considering the acetyl content of the surface of the board) is generated at the surface of the board, the distance to the surrounding acetylation liquid is much shorter, resulting in faster thermal exchange to the liquid.

#### ***Influence of acetic acid on the short-term strength properties***

The properties of the various categories investigated (treatment, drying schedule and acetic acid impregnation) are presented in Tables 5 (small stakes), and in Tables 6 and 7 for the large stakes.

**Table 5: Properties (averaged) of the small stakes (5 mm x 5 mm x 10 mm) for untreated and acetylated samples with various post treatments and drying schedules**

	Drying schedule	EMC at 65% RH. 20 °C [%]	Density [kg/m <sup>3</sup> ]	MOE [N/mm <sup>2</sup> ]	MOR [N/mm <sup>2</sup> ]
<b>Untreated</b>	-	12.5	592	9532	107.76
	Slow	11.2	578	8030	108.60
	Intermediate	10.8	590	8526	113.41
	Fast	11.6	586	8701	113.51
<b>Acetylated 3x steamed</b>	Slow	5.5	616	9752	126.18
	Intermediate	4.8	599	9205	120.98
	Fast	5.4	606	10036	130.67
<b>Acetylated 9x steamed</b>	Slow	5.9	588	8656	110.43
	Intermediate	5.6	593	8979	105.00
	Fast	5.3	592	9257	117.60

**Table 6: Properties (averaged) of the large stakes (20 mm x 20 mm x 350 mm) for untreated and acetylated samples with various post treatments and drying schedules**

	Drying schedule	AcoH% before drying [%]	AcoH% after drying [%]	EMC at 65% RH. 20 °C [%]	Density [kg/m <sup>3</sup> ]	MOE [N/mm <sup>2</sup> ]	MOR [N/mm <sup>2</sup> ]
<b>Untreated</b>	-	0.19	-	12.7	495	8234	74.82
	Slow	-	-	10.1	449	7902	75.31
	Intermediate	-	-	10.4	470	8057	78.16
	Fast	-	-	9.6	459	8061	74.26
<b>Acetylated 3x steamed</b>	Slow	9.74	0.76	4.8	512	8972	84.46
	Intermediate	9.74	0.51	4.8	480	7531	72.73
	Fast	9.74	0.09	4.6	488	8635	74.45
<b>Acetylated 9x steamed</b>	Slow	3.83	0.80	5.2	524	9117	87.46
	Intermediate	3.83	0.40	5.1	469	7718	76.82
	Fast	3.83	0.09	5.1	541	9402	83.25

**Table 7: Properties (averaged) of the large stakes (20 mm x 20 mm x 350 mm), impregnated with acetic acid, for untreated and acetylated samples.**

	Impregnated AcoH% [%]	AcoH% before drying [%]	AcoH% after drying [%]	Density [kg/m <sup>3</sup> ]	MOE [N/mm <sup>2</sup> ]	MOR [N/mm <sup>2</sup> ]
<b>Untreated</b>	0 %	-	-	439	8630	72.55
	3.5%	4.7	1.1	483	9209	79.32
	10 %	12.7	1.3	468	8976	78.55
	30 %	28.6	1.5	468	9151	77.33
<b>Acetylated 3x steamed</b>	0 %	-	-	516	9718	84.91
	3.5%	4.0	0.8	498	8794	69.97
	10 %	8.6	0.5	506	9136	81.27
	30 %	37.3	0.6	500	7727	83.10

For the large stakes (20 mm x 20 mm x 350 mm), no significant difference in the strength properties between the various post treatments and untreated and acetylated wood samples could be observed (Table 6). Also, impregnation with acetic acid, followed by drying, does not significantly change the MOE and MOR properties (Table 7) for the large stakes. When the small samples are considered, acetylated wood with 3x steaming as post treatment shows significant higher mechanical properties than untreated and acetylated wood with the post treatment “9x steaming” (Table 5). However, because of the small size, measurement errors increase, so decreasing the accuracy of calculations. Additionally, the size of the stake has influence on the distribution of liquids and heat during acetylation and drying. For example: the

acetic acid can be removed easier (and faster) for the small stakes during drying, compared to the large stakes.

It was expected to find a difference between the strength properties for untreated wood impregnated with different mixtures of acetic acid, since the acetic environment combined with the heat during drying could lead to degradation of the wood polymers. However, it is known from the literature (Skaar 1989) and also shown here (Table 6), that the hygroscopic nature of wood decreases when the wood is exposed to “high” temperatures. This decrease of equilibrium moisture content (EMC), which should result in increased strength properties, seems to be compensated by the degrading effect of the acetic acid. The strength properties of acetylated wood are also the result of positive and negative effects of the acetylation process, and the net result seems to be comparable to untreated wood. However, the effect of acetic acid on the mechanical properties on long term remains unknown, and would be worthwhile to investigate.

## CONCLUSIONS

The results from this investigation showed that in some cases the mechanical properties (MOE, MOR, compression parallel to the grain, Janka hardness and shear strength) were increased by acetylation, especially with Scots pine and poplar. On the other hand, the MOE and MOR radiata pine were decreased by acetylation. Almost no change in mechanical properties occurred after acetylation of beech. These “shifting” results can be explained by considering the various effects of the acetylation process on the strength properties. Negative effects on the mechanical properties are the relatively reduced fibre amount per cross section and the reduced degree of polymerisation of the acetylation medium. The lower equilibrium moisture content of acetylated wood effects the mechanical properties positively. The mechanical properties of acetylated wood are the net result of the negative and positive effects during the acetylation process. The effect of acetic acid on the mechanical properties on long term, however, are still unknown.

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## Wood Modification in Latvia

Andris Morozovs<sup>1</sup>, Aivars Aboltins<sup>2</sup>, Juris Zoldners<sup>3</sup>, Ivars Akerfelds<sup>4</sup>

<sup>1</sup> Latvia University of Agriculture, Liela iela 2, Jelgava LV3001, Latvia, andrism@cs.ltu.lv

<sup>2</sup> Latvia University of Agriculture, Liela iela 2, Jelgava LV3001, Latvia, aivars@cs.ltu.lv

<sup>3</sup> Latvian State Institute of Wood Chemistry, Dzerbenes iela 27, Riga, LV1006 medicami@edi.lv

<sup>4</sup> Latvian Association of Wood Processing Entrepreneurs, Skaistkalnes iela 1, Riga LV1004, ivars.akerfelds@kvc.lv

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### ABSTRACT

This paper describes developments in research and process development in wood modification in Latvia. Several wood modification processes have been developed at the Latvia State Institute of Wood Chemistry. One of them was wood treatment with ammonia in the liquid or vapour phase with subsequent densification or bending and drying of the treated material. The second one was wood impregnation with resin solutions (phenol-formaldehyde condensates or silicones) with subsequent curing in the wood structure. The third one was impregnation of wood with monomers, or their mixtures, with subsequent polymerisation by gamma-irradiation or thermochemical methods. The monomers used were: styrene, styrene mixtures with acrylonitrile, vinylacetate, sulphur dioxide, oligoesteracrylates, acrylic acid, methylmethacrylate and acrylic or methacrylic acid.

Decorative elements, flooring materials, insulating materials for electricity transfer lines; items for textile industry, gears, and some other items were produced from modified wood in experimental plant scale.

Solid wood acetylation with acetic acid anhydride and other reagents were studied in Latvia University of Agriculture. Magnesium perchlorate catalyst, dichloromethane vapours, water and high frequency current were studied to increase the acetylation degree of wood. Laboratory trials resulted in designing, making up, and putting in action pilot equipment for solid wood acetylation with acetic anhydride in the liquid phase. Different trials with various reagents and solvents were performed to fix or to extract residual acetic acid from solid acetylated wood. Impregnation of wood with acetic anhydride is one of main process determinative factors. A mathematical model describing acetic anhydride diffusion in wood was created.

### INTRODUCTION

Wood is readily degraded by different organisms. The main functional group in cellulose, hemicelluloses and lignin macromolecules is the hydroxyl group. It has property to form hydrogen bonds inside macromolecules, as well as to interact with other substances, for example, water, enzymes, *etc.* Any enzyme can be active, when the environment contains a sufficient amount of free water and a substrate, which contains active sites. Hydroxyl group polarity alteration can be carried out by its chemical modification. One such chemical modification method is acetylation. Since the acetyl group can be metabolised by different destroying



organisms: bacteria, fungi, pests, *etc.*, this ensures environment friendly wood protection against deterioration and allows for uncomplicated modified wood recycling process.

Wood shrinkage and swelling causes warping, bowing and cracking under changing humidity in wood products. Replacement of the hydrogen atom in the hydroxyl group of wood with an acetyl group having a different polarity affects the hydrogen bond network and decreases the ability of acetylated wood to swell in the presence of absorbed water.

## EXPERIMENTAL METHODS

### *Wood treatment with ammonia*

Birch, alder and pinewood were used for modification with ammonia. The modification process consisted of following stages: 1) Timber loading into an autoclave (10 m<sup>3</sup>). 2) Heating of the wood to a temperature of approximately 330 K. 3) Vacuuming. 4) Introduction of ammonia vapour into the autoclave. 5) Heating at 370 K. 6) Releasing of pressure to partially remove water and ammonia vapours from the autoclave. 7) Removal of the residual ammonia from the wood by vacuuming (0,01MPa). 8) Air was introduced into the autoclave before unloading of the wood. The duration of all the process was 4-8 h. Treated wood with definite moisture was processed by densifying in press to necessary density (600-1400 kg.m<sup>-3</sup>) or forming to required shape. For the fixation of the shape half-finished articles were dried at 370 K.

### *Modification of wood with vinyl monomers*

Different styrene mixtures with other monomers or oligomers (styrene with polyester resins, diethylene- or triethylene dimethacrylate, maleic anhydride) were used for wood modification. Azobisisobutyronitrile, isopropylbenzene hydroperoxide or dicumene hydro peroxide were used as polymerisation initiators in amounts of 0,5-1,2% of the monomer. Modified material was produced on experimental plant scale. Equipment consisted of an impregnation cylinder (1,5 m<sup>3</sup>), polymerisation cylinder (3 m<sup>3</sup>), heat exchanger, ventilator, tanks for components, reactor for mixing of the components and measuring devices. Birch, or alder wood was used for modification. Wood was impregnated with monomers by vacuum-pressure method. Depending on the density of the wood, the impregnated amount of the monomer was 0,6-1,4 kg/kg of wood. The polymerisation process consisted of the following stages: 1) Impregnated timber loading and closing of cylinder. 2) Cylinder flushing with carbon dioxide to prevent explosion and monomer oxidation. 3) Reactor ventilation and heating by gradually increasing the temperature in the wood blocks to 330 K. 5) Turning off the heating immediately after the beginning of the exothermic reaction. 6) Intensive cooling of the wood blocks when the temperature exceeded 360 –370 K. 7) Heating was turned on to maintain the temperature for several hours at 360 –370 K for the completion of reaction, when the temperature in the cylinder began to fall. 8) Cooling of the modified wood and unloading of the cylinder.

## RESULTS AND DISCUSSION

### *Wood treatment with ammonia*

Initially, wood on the experimental plant scale was treated with 25% ammonia solution, but then this method was rejected because of the necessity of removing a great quantity of water after treatment and, besides this, the modification cycle was too long. It should be noted that it is difficult to modify softwoods by ammonia treatment, because of insufficient plasticity after treatment. Softwoods were treated with ammonia mainly for deep coloration of the material. The mechanical properties of the ammonia-modified wood mainly depend on the density of the material (almost linear dependence was observed) and may be several times higher than that for

the initial wood. A disadvantage of the ammonia-treated wood is its insufficient form stability. In order to overcome this disadvantage, pressed or bowed wood items were heated at a temperature of 410-450 K for formation of new cross-links in the wood structure.

#### ***Modification of wood with vinyl monomers***

The main problem during wood modification with vinyl monomers is significant heat release during the polymerisation process, which is difficult to manage. In our equipment, it was achieved by very intensive gas circulation in the polymerisation cylinder and using wood blocks with cross-dimensions not exceeding 5-6 cm. After modification, wood usually contains 0,3-0,5% of residual monomer and for decreasing this amount, the material must be additionally stored for some weeks, or treated thermally. Besides the above described procedure, smaller scale treatments with glycerine, water, saturated salt solutions and urea solution were used as heat carriers for wood blocks with greater dimensions. In all cases, the outer layer of wood blocks (1-2 mm) must be removed before further utilisation. Several other modification processes at the institute were developed on a laboratory scale (modification with phenol-formaldehyde, resorcinol-formaldehyde, urea-formaldehyde resins, modification by gamma irradiation induced polymerisation of methylmethacrylate and mixtures, post-irradiating polymerisation and others).

#### ***Acetylation of wood in Latvia***

Professor Karlis Svalbe first studied modification of wood with acetylation with acetic anhydride at the Department of Chemistry of Latvia University of Agriculture. The main investigations on wood acetylation were performed in a period from the sixties until the beginning of the eighties (Svalbe, 2000). In the late nineties, the research on wood acetylation was renewed.

#### **Species, reagents, process conditions in acetylation of solid wood**

Pine (*Pinus sylvestris*), spruce (*Picea excelsa*), aspen (*Populus tremula*), birch (*Betula verrucosa*), grey alder (*Alnus incana*), black alder (*Alnus glutinosa*), oak (*Quercus robur*), ash (*Fraxinus excelsior*), maple (*Acer excelsior*), and linden (*Tilia cordata*) wood were acetylated mostly with acetic anhydride in liquid or vapour phase and with ketene. (Ozolina and Svalbe, 1969, Karlson and Svalbe 1977, Vitolins 1978). Process conditions depended upon impregnability and kind of reactant. Reaction rate and of acetyl group content for acetylation of wood with acetic anhydride vapour were higher than in liquid phase (Ozolina and Svalbe 1969). Equipment for acetylation of wood with acetic anhydride in the vapour phase was designed and constructed (Svalbe *et al.* 1982). A disadvantage of acetic anhydride modification is the production of equivalent moles of acetic acid as by-product, which is difficult to evacuate from solid wood.

Theoretically, no acetic acid is produced, when ketene is used as reagent instead of acetic anhydride, in the absence of water. Ketene was produced by pyrolysis of diketene and gave higher yields of acetyl groups. Hard woods were more reactive with ketene than soft woods. Optimal reaction temperature with ketene was determined as 320 K (Karlson *et al.* 1973a, Svalbe *et al.* 1973a, Karlson and Svalbe 1977). Ketene is very toxic and explosive. Ketene residue in the reaction chamber and acetylated wood was neutralised with ammonium (Karlson *et al.* 1976a). To reduce these risks, wood acetylation with diketene was investigated and mass percent gain by acetyl groups (MPG) of 35% at 325 K was obtained (Karlson *et al.* 1976b). The nature of mass increase in this case is unknown. Moisture content in wood samples from oven dried (0%) to 20% was varied to investigate the influence of wood moisture content on acetylation degree. Moisture content of pine softwood till 8 -10% had a positive effect on MPG yield. It was shown that practically, it is possible to acetylate softwood with moisture content until 14% (with acetic anhydride), 20% (with ketene). Moisture content of hardwood had no significant effect on MPG

(Karlson and Svalbe 1977, Vitolins 1978). Increase of sample size in radial and tangential direction from 5 to 40 mm diminished MPG from 26% to 18%. Increase of sample size in the longitudinal direction from 50 to 250 mm diminished MPG from 25% to 17% for acetylation with acetic anhydride. It was necessary to increase impregnation time with acetic anhydride and reaction temperature to achieve a MPG of 20% (Vitolins 1978). Increase of wood samples with crosscut size 10 × 10 mm in fibre direction length from 10 to 150 mm reduced MPG 3 times in average with all investigated species of wood in case of acetylation of wood with ketene (Karlson and Svalbe 1977).

It was shown that reaction time could be reduced when an oven with current frequency in 21-25 MHz range was used as the heater for wood modification with liquid acetic anhydride. Acetylation degree of 20 -24% was reached with high frequency heating after 30 – 40 minutes, compared to 6 hours by convection heating (Klotins *et al.* 1973, Svalbe *et al.* 1973b, Svalbe 1983).

A MPG 21% of acetylated wood could be reached in one third of the time, when 0.1% magnesium perchlorate solution in acetic anhydride was used for acetylation of pine sapwood, in comparison with acetylation without catalyst. Acetylation of pine sapwood with acetic anhydride in the presence of 0.5% of magnesium perchlorate solution gave a MPG of 35%. Such MPG of acetylated wood was not possible to get with acetic anhydride without a catalyst. Disadvantages of use of magnesium perchlorate, as catalyst are very strong oxidising properties, which can induce oxidation of the wood and reduce mechanical properties of acetylated wood (Ozolina and Svalbe 1972, Svalbe *et al.* 1974, Truksne and Svalbe 1977).

Some species of wood are hard to impregnate with acetic anhydride (spruce, pine heart wood, etc.). Acetone, dioxane, ethanolamine, and their 10% solutions in dichloromethane were examined to improve impregnation properties of wood with acetic anhydride by swelling of wood in these solvents before acetylation. Treatment of wood with a vapour of dichloromethane before acetylation was very efficient and gave an increase in MPG (until 9%). Less effect was reached with liquid methylene chloride. Indeterminate increase in MPG was achieved with ethanolamine (Svalbe *et al.* 1979).

The main goal of the investigation was to design technological process for wood acetylation on an industrial scale. On the basis of laboratory research results, pilot-scale equipment was designed (Vitolins 1978). Such equipment was constructed and put into action at the Krilov institute in Leningrad (now St. Petersburg, Russia) in co-operation with Russia engineers. Two parallel acting acetylation reactors, containers for reagent and by products, pipes, and valves were made from stainless steel. Maximal length of timber that could be acetylated was 3 meters. Different schedules were investigated (Burlakov *et al.* 1973 and 1974, Nikitina and Otlesnov 1976, Otlesnov and Nikitina 1977).

### **Acetylation of wood fibre**

A wide range of investigations on wood pulp acetylation with acetic anhydride (Kuka 1983, Ozolina 1983, Ozolina *et al.* 1973, 1974a, b, Svalbe 1985, Svalbe *et al.* 1973c, 1975a,b) and ketene (Karlson 1973b) was carried out. To remove acetic acid from acetylated wood, the fibre was treated with acetylene after acetylation (Ozolina *et al.* 1974a). The fibre boards were manufactured from acetylated wood pulp without any adhesive (Ozolina *et al.* 1973 and 1974a, b, Svalbe *et al.* 1973c) or using polyvinyl acetate emulsion (Svalbe *et al.* 1975a) or hexamethylene diisocyanate (Svalbe *et al.* 1975b) as adhesive. The hydrophobic properties of fibre boards were improved by moistening the fibre mat to 7 – 22% before pressing (Ozolina *et*

*al.* 1974a). The swelling of wood fibre boards, processed from the acetylated wood fibres was six times less than boards made from natural wood pulp. Fibre boards of acetylated wood were resistant to *Coniophora puteana*. The acetylation of intact fibreboard instead of pulp, was also investigated (Svalbe *et al.* 1973d).

#### ***Treatment of modified wood to improve properties of final product***

Complete removal of acetic acid from acetylated wood from is impossible (Kuka and Kuka 1983), because it is fixed by chemical sorption in acetylated wood. Several methods for chemical conversion of remaining acetic acid were therefore investigated. The bulk acetic acid can be evacuated by means of cyclic vacuum – pressure impact at elevated temperature. Residual acetic acid can be neutralised only with chemical treatment. In this regard, acetylated wood was treated with acetylene for 1 –8 hours at 352 – 392 K and a pressure of 0,15 – 0,4 MPa (Svalbe *et al.* 1975c) or extracted several times with dichloromethane (Svalbe *et al.* 1978), or hot water (Burlakov 1973). Acetylated wood after evacuation of bulk acetic acid was impregnated with ethylene oxide for 2-4 hours at 320 – 330 K (Svalbe *et al.* 1976). Impregnation for several times with 5-10% octadecylamine (C<sub>18</sub>H<sub>37</sub>NH<sub>2</sub>) solution in dichloromethane was examined (Svalbe *et al.* 1979).

Impregnation of acetylated aspen, birch, pine and larch woods with polyethylene glycol (molecular mass 1500 or 15000) solution in water gave near 100 percent anti-swelling efficiency. Polyethylene glycol up-take varied from 49 to 66% (Vitolins 1978 Svalbe *et al.* 1983).

Acetylated birch impregnation with oligomers of phenol formaldehyde resins (phenol alcohol) under pressure with phenol alcohol solution uptake 90 - 100% and pressing till density 1200 kg.m<sup>-2</sup> was reached. Pressed wood samples were heated 4 h at 410 – 415 K to polymerise phenol alcohol. Modified wood had better physical mechanical properties than impregnated and pressed samples without acetylation (Shamajev, 1990).

With the aim of improving water-repellent properties, impregnation of acetylated and natural wood with rapeseed oil, or ethyl esters of fatty acids was studied. Acetyl groups gave the main improvement in anti-swelling efficiency (ASE). Impact of hydrophobic fatty acid radicals was less. Improvement of ASE was permanent only when acetylated wood was treated. Impregnation of natural wood with plant oil or ethyl esters did not change ASE and only reduced water absorption by a bulking effect. The difference in interaction of acetylated wood and natural wood with oil or rapeseed oil ethyl ester is due to the lower polarity of acetylated wood (Morozovs 2001a, b, Morozovs and Aboltins 2000a).

Acetylated with ketene wood impregnated with a saturated solution of ammonium phosphate, had a MPG of acetyl groups of 21 – 24%, MPG of phosphates 12 – 14%, water absorption 54 – 57%, moisture absorption around 6%, and swelling in water less than 2% (Karlson 1981).

Wood acetylated with ketene to a MPG of acetyl groups 12 – 15% was impregnated with methacrylic acid triethylenglycol ester. Polymerisation was initiated by  $\gamma$ -radiation. Acetylated wood filled with polymer had better physical and mechanical properties (Karlson *et al.* 1973c and 1975).

Birch wood with a moisture content of 8% was placed in an autoclave and treated with ammonia under a pressure of 0,15 MPa to MPG 5%. Treated wood was aerated, acetylated and pressed at 3 MPa for 0,5 h. Control examples were treated in an analogous way but without acetylation. Acetylation diminished water absorption and swelling (Grinberg *et al.* 1974).

***Properties of acetylated wood***

Acetylated wood (with different degrees of acetylation) exposed in contact with *Coniophora puteana* exhibited no statistically significant mass loss when the acetylation degree (MPG) was above 20% for pine, 15% for aspen and birch, and 12-13% for lime wood. Tests with termites were carried out in termite hills in Turkmenistan showed that white ants did not attack acetylated wood with a MPG above 20% (Truksne and Svalbe 1977, Vitolins *et al.* 1968a, b).

Acetyl groups resistance against hydrolysis in water was examined at temperatures from 310 to 373 K. Acetyl groups content decrease did not exceed 1,6% after 1 month (Truksne and Svalbe 1977, Vitolins *et al.* 1968a, b, Rugevica *et al.* 1977). Acetylated and natural pine, aspen, birch and lime-tree wood samples were immersed in water at room temperature for 1 month. The swelling dynamics of wood samples was examined. Acetylated wood swelled 2,5-3,5 times less than natural wood. Pine sapwood acetylation reduced the difference between swelling in tangential and tangential direction from 38% to 12 – 15%. Acetylation had less effect on anti-swelling properties of aspen wood (Truksne and Svalbe 1977, Vitolins *et al.* 1968a, b, Rugevica *et al.* 1977).

Testing of phenol-formaldehyde, resorcinol-formaldehyde or urea-formaldehyde adhesives for acetylated and natural wood gluing showed that in wet conditions, the urea-formaldehyde resin joint was two times weaker than glued joints with phenol and resorcinol resins. No significant difference was noted between acetylated and natural wood glue joints in dry conditions. Acetylated wood showed less glue strength losses than natural wood, after 48 h soaking in water.

***Investigation of wood acetylation chemistry***

Acetylation degree of acetylated wood mainly was determined by difference of mass of sample before and after acetylation (MPG). It was controlled by parallel determination of acetyl group content before and after reaction by hydrolysis of the wood in sodium hydroxide solution and titration of the base excess. Absorption of the carbonyl group of the acetyl group in the IR region was chosen to estimate acetylation degree. Correlation between IR absorption of carbonyl groups of ground wood samples powdered with dry potassium bromide and MPG of acetylated wood was stated (Kuka 1993, Kuka and Kuka 1995).

Probability balance experimental design plans were used to evaluate the significance of 9 parameters influencing degree of acetylation of ground wood (Morozovs 1983) and solid wood (Ancans *et al.* 1998). Linear effect, double and three fold interactions of factors in solid wood acetylation were evaluated. Statistically significant was the influence of factors that are dependent upon diffusion processes (Ancans *et al.* 1998).

The wood acetylation process can be divided into two stages: diffusion of acetic anhydride in wood and chemical reaction between acetic anhydride and wood. Acetic anhydride and acetic acid vapour diffusion in acetylated birch and pine wood particles were studied and sorption velocity of acetic acid and acetic anhydride vapours were measured. Wood absorbed acetic acid vapours in greater extent than acetic anhydride (Kuka and Kuka 1995).

The first stage of wood acetylation – impregnation of wood with acetic anhydride is the main factor that affects the process. Statistical analysis of data of liquid acetic anhydride permeation in wood samples in immersion conditions or contacting the crosscut end with acetic acid anhydride at room temperature showed that wood impregnation with acetic anhydride depended upon density of wood and duration of treatment (Morozovs *et al.* 1997a and 1998).

Mathematical models of acetic anhydride diffusion in wood in the fibre direction and in the fibre and perpendicular directions were proposed. The proposed models can be applied for investigation of acetic anhydride mass transfer in solid wood (Aboltins and Morozovs 1998, 2001a, b and 2002, Aboltins *et al.* 1999, Morozovs 1997b, Morozovs and Aboltins 1999, 2000b and 2002, Morozovs *et al.* 1997a, b).

#### ***Application of modified wood***

The greater part of ammonia-modified wood was used for production of flooring. The second widely used application was different decorative interior elements and furniture elements (for example, chairs). Besides this, such wood was used for production of handles, sports accessories, rifle butts, and some machine elements (gears, bearings). Birch logs treated by ammonia were peeled and veneer of 15 mm thickness was produced. By means of hot rolling, the material was densified and thickness reduced to 7-8 mm, this product was used for parquet block upper layers. Birch or white alder wood modified by ammonia and then densified, produced so called "lignamon", this material sawed in strips of thickness 7-8 mm was used *e.g.* in the upper layer of covering shields for telecom cable channels.

Peeled birch, white alder veneer modified by ammonia was used to produce decorative veneer; this product was used in upper layers of plywood products for decorative purposes. The wood modified with vinyl polymers was used for production of bobbins for the textile industry, elements for electric-transfer lines and flooring. Modified wood items in all cases served several times longer, than items from the same unmodified wood. Acetylated wood was used in ship designing. At present there is one high temperature wood thermal treatment production unit working in Latvia

### **CONCLUSIONS**

Birch, alder or pinewood was modified with ammonia at 370 K. By treatment with ammonia, hardwoods can be pressed or formed to any desired shape. The mechanical properties of the ammonia-modified wood mainly depend on density and may be several times higher than for the untreated wood. A disadvantage of the ammonia-treated wood is its poor form stability.

Vinyl polymer modified wood in all cases served several times longer, than unmodified wood.

Acetylation of 10 species of wood showed that the acetylation process with acetic anhydride and ketene could be adjusted for each wood species. Ketene has a higher reactivity with wood. Moisture or polar solvent facilitates wood's hydroxyl groups' reactivity with acetic anhydride and ketene. Acetylation time of wood can be reduced with high frequency current heating. Magnesium perchlorate catalyst increases acetylation degree of wood with liquid acetic anhydride. Laboratory trials resulted in designing, making up, and putting in action pilot equipment for solid wood acetylation with acetic anhydride in the liquid phase. The fibre boards without any adhesive could be manufactured from acetylated wood pulp or small particles. Treatment with various reagents is recommended to reduce acetic acid content in acetylated wood. Acetylation in combination with impregnation with polyethylene gives completely form-stable modified wood. Acetylated wood with a content of acetyl groups higher than 20% is stable to *Coniophora puetana*. Such wood has 3,3 – 3,6 times less moisture absorption and reduced by 40% water absorption. Swelling in the radial direction is reduced 3,6 and in tangential – 5,5 times in comparison with natural wood. A mathematical model of acetic anhydride diffusion in wood was proposed.

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**SCALING UP AND MARKETS**  
POSTER PRESENTATIONS



## Melamine Modification of Acetylated Spruce Wood

Christian Hansmann<sup>1</sup>, Wolfgang Gindl<sup>1</sup>, Fariborz Zargar-Yaghubi<sup>1</sup>  
and Rupert Wimmer<sup>2</sup>

<sup>1</sup> Competence Centre for Wood Composites and Wood Chemistry, Institute of Wood Science and Technology, BOKU - University of Natural Resources and Applied Life Sciences, Gregor Mendel Straße 33, A-1180 Vienna, Austria, email: hansmann@mail.boku.ac.at

<sup>2</sup> Competence Centre for Wood Composites and Wood Chemistry, Institute of Botany, BOKU - University of Natural Resources and Applied Life Sciences, Vienna, Austria

**Keywords:** acetylation, melamine, UV-microscopy, compression strength

### ABSTRACT

Acetylation and melamine resin impregnation has shown considerable potential to improve a number of wood properties, among dimensional stability and surface hardness. A combination of these two modification methods may lead to a product that shows the advantages of both. In this study, the uptake of melamine resin into cell walls of acetylated spruce wood and effects of this treatment on compression strength perpendicular to grain were studied. For this purpose, spruce samples were infiltrated with a melamine resin after acetylation to various weight gains. Using the high absorbance behaviour of melamine in ultraviolet light, spectra were recorded with a Zeiss MPM 800 spectrophotometer microscope at measuring spot sizes as small as 1 µm. Transverse sections with a thickness of 1 µm were prepared from the specimens after embedding in epoxy resin. Taking advantage of the proportionality between resin concentration and absorbance, estimates of melamine concentrations in the cell walls were possible. To express the amount of resin penetrated into cell walls, a spectral quotient of the absorbances at 241 and 281nm was defined, the assumed maxima of melamine and lignin, respectively. Acetylation to various weight gains prior to melamine impregnation did not significantly affect melamine uptake into cell walls. As a conclusion, a combined treatments will not suffer from any negative drawbacks. Compression tests normal to the grain were performed and large increases in compression strength as well as modulus of elasticity (MOE) were seen after melamine impregnation. The acetylated specimens seemed to have increased in brittleness compared to the unacetylated reference.

### INTRODUCTION

Besides superior material properties of solid wood, *e.g.* favourable mass/strength ratio, low thermal conductance, neutral carbon dioxide balance, pleasing visual appearance, there are existing disadvantages such as dimensional instability with changing moisture or unsatisfying mechanical properties perpendicular to grain. These properties may be altered by *e.g.* acetylation for improved dimensional stability (*e.g.* Rowell and Ellis 1978, Militz 1991, Rowell 1996) and melamine impregnation for increased surface hardness (Miroy 1995, Gindl and Gupta 2002). Melamine impregnation may take place in the cell wall with no resin-filled cell cavities, which maintains the porous character of wood. The combination of both modification types could lead to a product showing both improvements. However, the two treatments may interact negatively in a way the preceding acetylation lowers the potential for melamine to penetrate cell walls. The present work is part of a larger study and evaluates the penetration of melamine resin into acetylated cell walls. In addition, the consequences of combined modifications on the mechanical properties perpendicular to the grain were also tested.

## EXPERIMENTAL METHODS

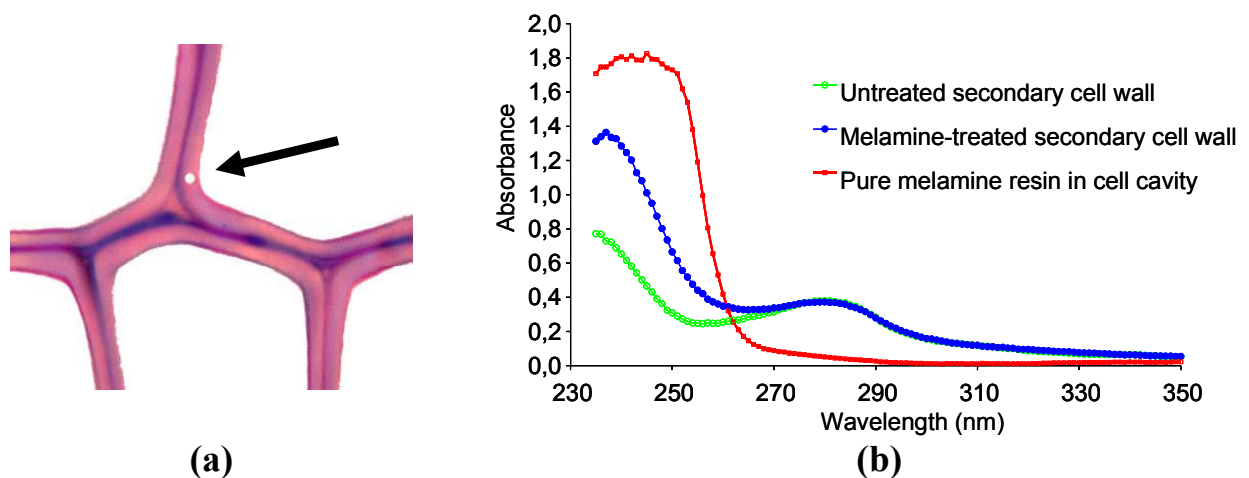
### *Acetylation and impregnation with melamine resin*

For the determination of the melamine content in cell walls, small pieces (3x5x1mm (RxTxL)) of spruce wood (*Picea abies* [Karst.] L.) were cut from the same sample, so that all specimens contained the same annual growth ring. Two groups were acetylated with a novel anhydride-reagent to a weight gain (WPG) of 3-4% and 19%, respectively. Another group was acetylated with the classical reagent acetic anhydride to a WPG of 26%. A third group were used untreated as a reference. For mechanical testing, specimens of 30x12x10mm (RxTxL) in size were cut from spruce wood (*Picea abies* [Karst.] L.). One set was acetylated with the novel anhydride-reagent (WPG=21%), another set was acetylated with acetic anhydride (WPG=21%), and a third one again remained untreated.

The melamine resin (MER®, AGRO Linz Melamin GmbH), which comes in solid state and is insoluble in water, was dissolved in methanol at a weight ratio of 1:1, with the aid of an ultrasonic bath. To ensure optimal penetration of the resin, the specimens were saturated with water, which was then exchanged 4 times for 2 hours. The impregnation technique was simple immersion at atmospheric pressure. The specimens for the determination of the melamine content in the cell wall were impregnated for 0, 1 and 20 hours, respectively, those for mechanical testing an extended period between 0 and 3 days, due to bigger sample sizes. After impregnation, the resin was cured at 180°C for 10 and 30 minutes, respectively, whereas the mechanical testing samples were dried overnight at 60°C, prior to impregnation. The reference-specimens underwent identical treatment with the exception of melamine impregnation.

### *UV-microphotospectroscopy*

After polymerisation of the melamine resin, the specimens for determination of the melamine content in the cell wall were dehydrated in a graded ethanol-acetone series and embedded in Spurr's resin (Spurr 1969). Cross sections with a thickness of 1µm were made with a ultramicrotome and quantitatively examined in the microphotometer microscope MPM 800 (Zeiss) for melamine detection in single cell walls, as shown by Gindl *et al.* (2002). Using a measuring-spot size of 1µm diameter (Fig. 1a), absorbance spectra of the S2 layers of early wood tracheids were determined (Fig. 1b).



**Figure 1:** Cross- section through spruce tracheids with a measuring spot (arrow) of the photometer microscope (a) and UV-absorbance spectra of untreated and melamine-treated secondary walls, as well as pure cured melamine resin in a cell cavity (b)

The high absorbance of melamine and lignin in the ultraviolet spectra range with characteristic maxima at 241nm over 281nm were utilised (Fig. 1b). Melamine concentration in the cell wall was estimated because of the proportionality between resin concentration and absorbance, at assumed constant lignin content (Gindl et al. 2002).

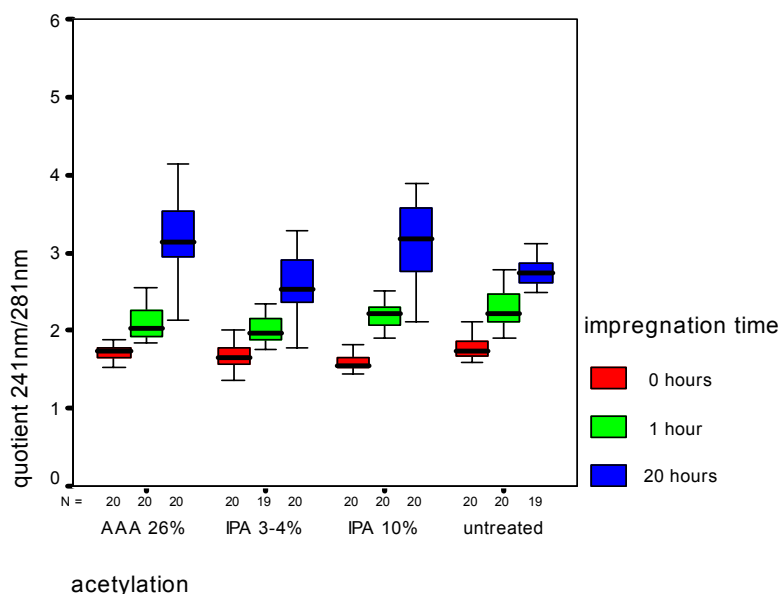
### ***Mechanical testing normal to grain***

After polymerization of the melamine resin, the specimens for mechanical testing were stored in an exsiccator above silica gel to hold their dry condition. Radial compression tests were performed on a Zwick UPM 100kN universal testing machine. The load was applied at a constant displacement rate of 0,5mm/min and clip-on strain gauges picked up the actual sample displacement during load.

## **RESULTS AND DISCUSSION**

### ***Melamine content in the cell wall***

Figure 2 depicts the variability of the ratio of absorbance at 241nm over 281nm as a relative measure of melamine content. It is clearly seen that after impregnation times of 1 and 20 hours, respectively, the selected melamine resin penetrates well into the cell walls, independent of the degree of acetylation.



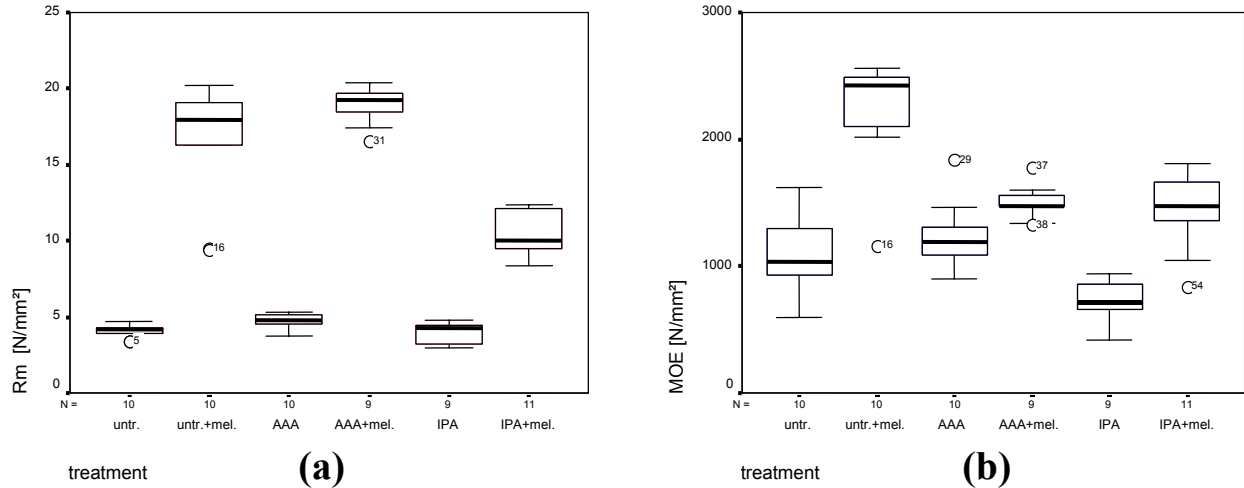
**Figure 2: Relative concentration of melamine in spruce cell walls (expressed as ratios of absorbance at 241nm over 281nm; earlywood) of differently treated samples (AAA 26% = acetic-anhydride-acetylated, WPG=26%; IPA 3-4% = acetylated with a novel anhydride reagent, WPG=3-4%; IPA 10% = acetylated with a novel anhydride reagent, WPG=10%; treatment duration 0, 1 and 20 hours)**

After 20h impregnation, it seems that acetylation even favours the uptake of melamine, which could be due to the non-hydrophilic nature of the MER resin used, as it is known that acetylation reduces hydrophilicity in wood (Sinn *et al.* 2002).



**Compression strength and MOE normal to grain**

Figure 3 shows a dramatic increase of both, compression strength (Fig. 3a) and MOE (Fig. 3b) after melamine modification. While MOE rose by percentages between 121% and 208%, compression strength even improved up to 408%.



**Figure 3: Compression strength (a) and MOE (b) normal to grain (same abbreviations as in fig. 2, WPG=21% for both, AAA and IPA)**

**CONCLUSIONS**

The presented data clearly demonstrate that a combination of acetylation and melamine impregnation does not interfere. Melamin impregnation has led to significantly improved MOE and compression strength normal to grain. The combined application of the two methods seems to be promising, especially with respect to bulk modification by acetylation and surface hardening by melamine treatment.

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## Modifying Plywood Raw Materials for a Stable, Fire Resistant Product

B. Tjeerdsma<sup>1</sup>, D.Jones<sup>2</sup>, W.Homan<sup>3</sup> and M. van der Zee<sup>4</sup>

<sup>1</sup> SHR Timber Research, Wageningen, the Netherlands, b.tjeerdsma@shr.nl

<sup>2</sup> Building Research Establishment, Centre for Timber Technology and Construction, Watford, WD25 9XX, United Kingdom, jonesd@bre.co.uk

<sup>3</sup> SHR Timber Research, Wageningen, the Netherlands, w.homan@shr.nl

<sup>4</sup> SHR Timber Research, Wageningen, the Netherlands, m.vanderzee@shr.nl

**Keywords:** mechanical properties, acetylation, process influence, acetic acid, pilot plant scale

### ABSTRACT

The demands of today's market requires products that have good a service life, represent value for money and offer as high a safety standard as possible. Within the composite industry (including the plywood industry), this includes developing improved fire retardant treatments. Whilst plywood is fairly resistant to combustion due to its construction, additional protection is necessary within the ever-increasingly stringent customer and insurance demands. To this end, a project is being undertaken in The Netherlands to investigate alternative methods for fire retardant treatments, whereby a greater emphasis is placed upon chemical bonding of the treatment to the wood. This will results in less leaching effects. Results of preliminary work are given, which show that improvements with the range of agents tested in this first trial using solid wood provided some degree of fire resistance, as well as improvements to some of the general properties also tested. It is postulated that these treatments can readily be applied to veneer, with these treated veneers then being used in the production of plywood with increased fire resistance.

### INTRODUCTION

Today's construction market utilises a wide variety of timber-based materials depending on the required uses. These include both solid wood and board products, the latter group including such materials as MDF, OSB, and Plywood to name but a few.

As with any other wood product, plywood is classified as a combustible material. Typically the ignition temperature is around 270°C if exposed directly to a flame. If not, ignition normally does not occur until temperatures of around 400°C have been reached. However, the performance of plywood in the event of a fire is usually very high, as the surface of the plywood is carbonised, which has the effect of protecting the panel and slowing down the burning process.

It is well known that fire retardants act by reducing the temperature at which the pyrolysis reactions occurring during combustion actually occur. This is achieved through the increasing of char formation during the initial stages of combustion, as well as helping to reduce the amount of volatiles released during these early stages (Le Van and Winandy 1990). It is these volatiles that help to accelerate the combustion process, as they provide amore readily ignitable material.

The effectiveness of many of the treatments currently used (for example systems based on phosphate or borate salts) depend upon the acidity of the said treatment. More acidic treatments tend to provide greater protection (Shafizadeh 1984), and are advantageous due to low cost. There is a downside to such treatments, this being the reduction in strength of treated products.

Such reductions in the strength of plywood may be accentuated by climatic conditions, especially elevated temperatures and high humidities (Le Van *et al.* 1990, Winandy *et al.* 1991, Winandy 1995). A recent study (Lebow and Winandy 1999) showed that dramatic strength reductions were realised after 60 days exposure to high temperature, this being attributed to the conversion of the monammonium phosphate into phosphoric acid. This was evident from pH studies, which showed that acidity increased from approximately 6.0 (for untreated plywood) to about 2.8 for samples treated with monoammonium phosphates and then exposed to an elevated temperature of 77°C for 49 days.

Apart from the problems with such current treatments with strength properties, there are also inherent problems with leaching of many fire resistant treatments. This could lead to secondary problems associated with the increased awareness of environmental protocols and pollutant control. To this end, work has been going on at SHR in The Netherlands to consider the potential of fire retardant treatments that are chemically bound to the wood.

### MODIFYING AGENTS

There are two forms of reagent that need to be considered within this subject, namely those that react directly with the cell wall, and those that undergo self-bonding / polymerisation to become trapped within the lignocellulosic matrix.

For the initial part of this project, a range of different reagents was considered. Due to the commercial sensitivity of these materials, the full names and structures cannot be given at present. Suffice to say each of the tested reagents represent organophosphate compounds. The reagents tested in this preliminary study were:

- ◆ BTC
- ◆ PC
- ◆ PPC
- ◆ DPN

### MATERIALS AND METHODS

For all experiments within this study, Scots pine sapwood (clear samples) was used. In order to achieve as effective a treatment as possible, all initial tests were carried out with solid wood. Once suitable methods had been identified, these would then be applied to veneer prior to the manufacture of plywood. Treatments were carried out as shown in table 1.

*Table 1: Tested Combinations of phosphor containing chemicals and the concentration of treatment*

Chemical	0 %	1 %	2.5 %	5 %	10 %
PC			X		X
PP		X	X	X	X
DPN			X		X
BTC			X		X
Blank	X				

The dimensions treated and subsequently tested depended upon the standard test being investigated (table 2). MOR / MOE measurements were carried out as according to standard, whilst the other tests used in-house testing conditions developed by SHR.

Table 2: Standard tests carried out following treatment

Tested parameter	Test Specimen Dimension [mm]	Total No. of Samples	Results rounded off
Burn Test (WVS-SHR/064)	30 * 10 * 100	5	Y
Dimensional Stability (ASE) (WVS-SHR/048, 049)	30 * 30 * 10	10	N
Breaking Strength (MOR)	5 * 10 * 100	10	Y
Modulus of Elasticity (MOE)	5 * 10 * 100	10	Y
Durability according to EN807	5 * 10 * 100	3 * 10	N
Equilibrium Moisture Content (EMC) (WVS-SHR/047)	30 * 30 * 10	10	N
Leaching Test (WVS-SHR/063)	30 * 30 * 10	10	N

## RESULTS AND DISCUSSION

In terms of the burning tests, it can be seen that the treatments tested provide some degree of protection compared to the untreated samples (figure 1). With these burn tests following the removal of the flame, it was found that burning continued for less than 15 seconds with all treatments at maximum level of treatment (10%), whereas the untreated samples continued to burn for almost a minute. For each treatment (with the exception of PPC), it can also be noted that there is an improvement in effectiveness of treatment as the percentage loading increases, as might be expected. The results for PPC at 5% treatment level are confusing, and it is thought that these represent an experimental error. Further tests are being carried out to confirm this.

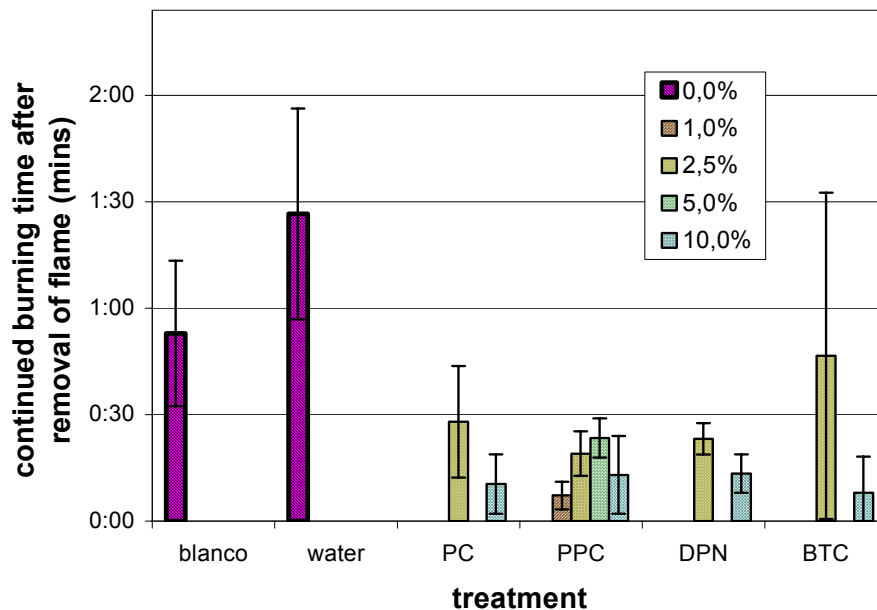
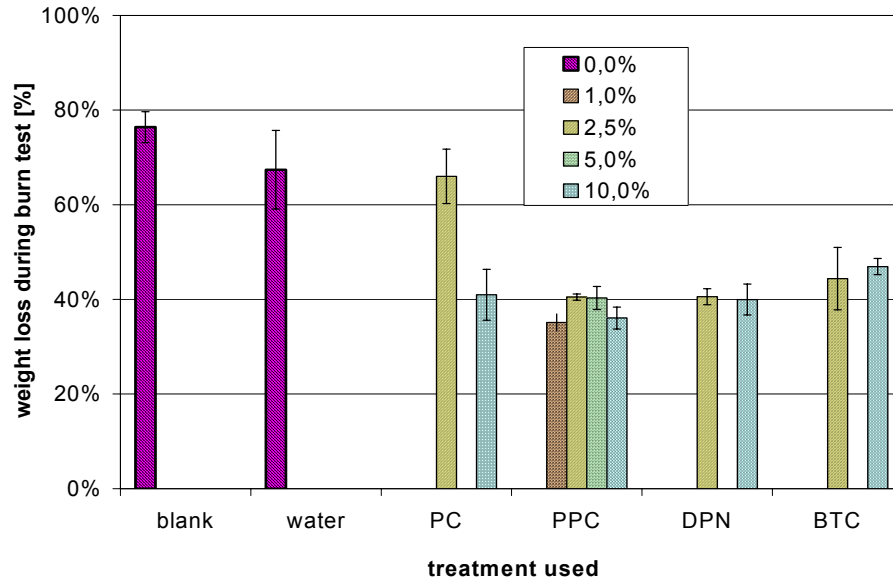


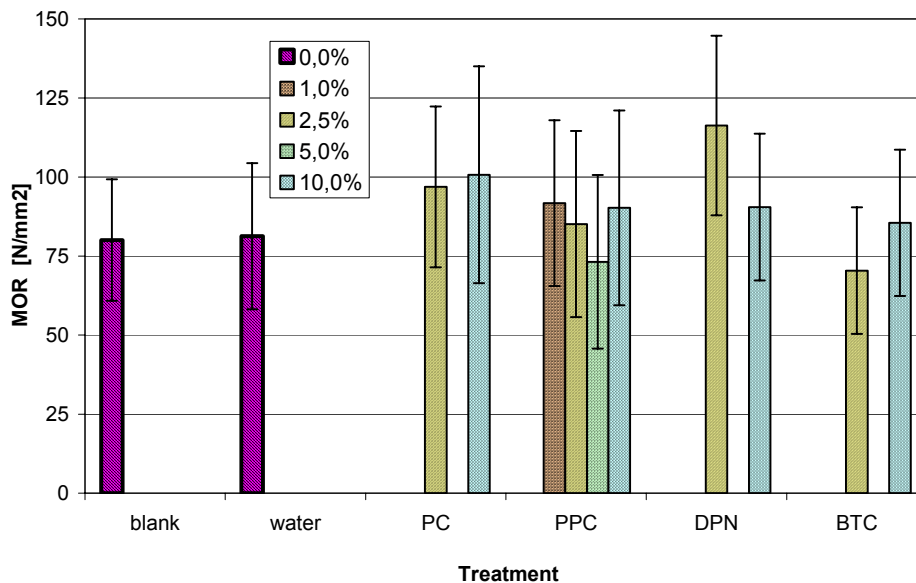
Figure 1: Effect of treatment on the continued burning time following removal of flame.

Further information may also be gained from the weight loss following the burning test. Here (figure 2) it can be seen that a considerable improvement in the sample remaining following the burn test for all reagents tested, though the results for PC proved to be not as effective when treated at low levels. In general, it can be seen that improvements of between 70 and 90% in the amount of material lost can be achieved through the addition of these treatments.



*Figure 2: Degree of weight loss measured following exposure to a flame for 3 minutes followed by continued combustion for a further 2 minutes.*

In order to assess if a treatment has been effective, it is necessary to consider all aspects of behaviour of the treated wood. Thus a series of tests were carried out to ascertain any effects on the mechanical properties of the wood. Figure 3 shows how the mechanical strength was affected following treatment. Here it can be seen that three of the treatments resulted in increases in the MOR values, whilst treatment with BTC resulted in an equal / slightly reduced value for the tested samples. In the case of DPN, an improvement in MOR values of approximately 50% could be gained.



*Figure 3: Mechanical strengths of treated samples*

Similar results were found when investigating the modulus of elasticity. Here, all treatments enhanced the MOE values beyond those of the untreated samples. Hence it would seem that such treatments would have no detrimental effect on the overall mechanical performance of materials treated in this way.

Another key aspect to assessing if a chemical treatment is successful is by its effect on the dimensional stability of the wood. The most recognised method of showing this is through the anti-shrink efficiency (ASE) value. Each treatment tested resulted in slight increases in the ASE values, these increasing with higher levels of treatment. Naturally the higher the ASE value the more dimensionally stable the material, and hence the more desirable the reaction. This would indicate that treatments at the 10% level would appear more advantageous, and especially those for PPC and DPN. However it should be noted that these values are still considerably lower than those for conventional chemical modification reactions (*e.g.* acetylation) where ASE values approaching 70% may be easily achieved, and even as high as 90% (Hill and Jones 1996).

With treatments such as acetylation, reactions within the wood cell components result in the hydroxy groups present reacting with acetic anhydride in such a way as to esterify these hydroxy groups. The net effect of this is to increase the hydrophobicity of the wood. This is due to there being less hydrogen bonding possible to moisture. Thus the equilibrium moisture content for acetylated wood is lower than untreated samples. The treatments used in these experiments all contain carbon chains which could act in a way similar to the acetyl group. However the phosphate groups also introduce an alternative group capable of undergoing hydrogen bonding with moisture. In order to see if there would be any effect of the equilibrium moisture content, a series of tests were carried out (figure 4). These show that the treatments used in this study did result in an increased EMC for the wood samples. Thus there would seem to be a greater affinity to moisture. This fact combined with the results already indicated from work on the dimensional stability suggests that the wood is in a permanently swollen state. The treatments used have the effect of increasing the hydrophilic nature of the wood as well as increasing the number of incumbent sites in the wood capable of undergoing hydrogen bond interactions with moisture.

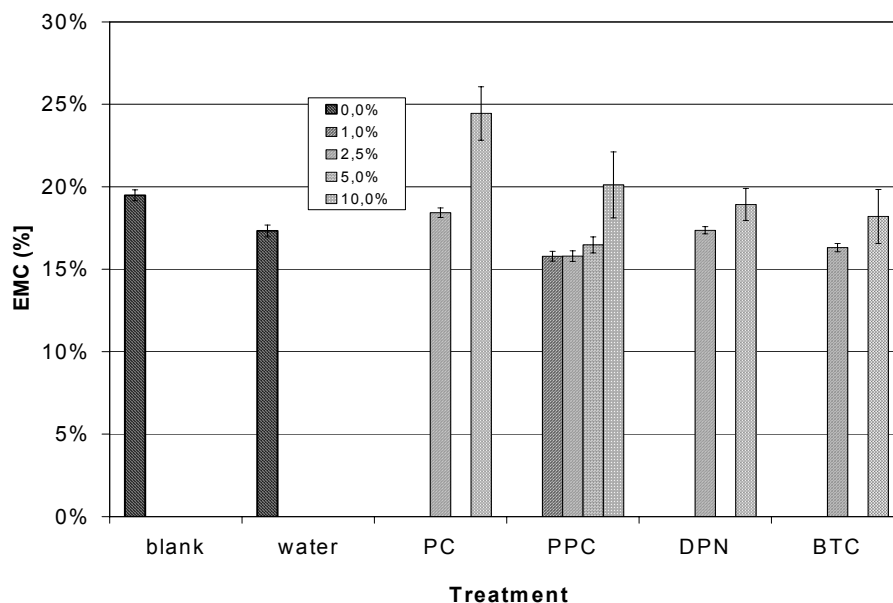


Figure 4: Equilibrium moisture content (EMC) values for samples at 90% relative humidity



In addition to these tests, an initial evaluation of the biocidal effect of the treatment was undertaken, through the use of an ENV807 test. Results from this (shown in Figure 5) indicate that the treatments tested do indeed reduce the weight loss following exposure for 8 weeks, with these weight reductions in general being between 50 and 65%. It is interesting to note that for the lower treatment level with DPN no benefit was noted, though the higher level resulted in the most effective treatment. Thus there would seem to be a threshold above which the use of DPN becomes effective. This threshold limit was not found for PPC, which was equally effective at all treatment levels, with a reduction in weight losses of around 65% for each of the treatment levels considered.

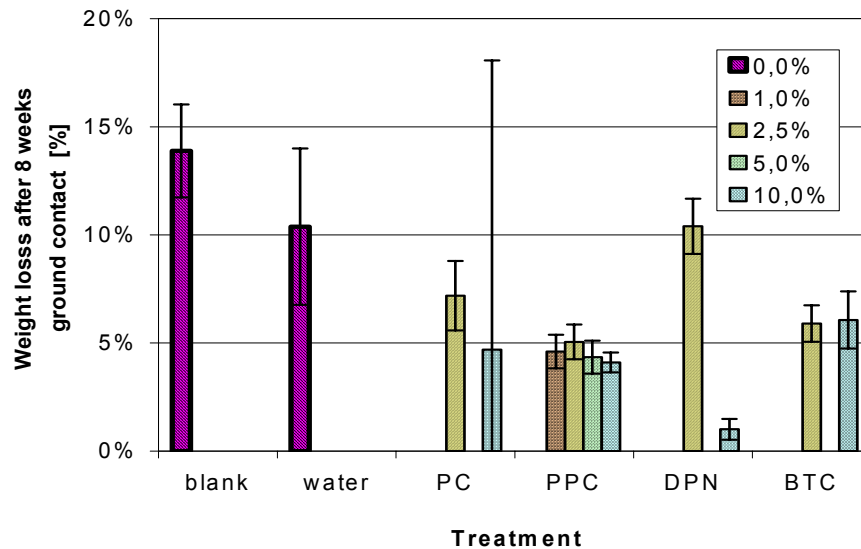


Figure 5: Weight losses following ground contact testing for a period of 8 weeks

## CONCLUSIONS

The role of organophosphate agents has been investigated as potential reagents for increasing the fire resistivity of solid wood and wood products. Initial work has focussed on testing solid wood, and this has shown that each of the treatments investigated were capable of improving the performance of the wood to some degree for all the test methods carried out. These treatments offer potential for further development and will be the focus for further research, especially for panel products.

## ACKNOWLEDGEMENTS

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**ENZYMATIC TREATMENTS**  
ORAL PRESENTATIONS



## Laccase Catalysed Enhancement of the Autoadhesion of TMP fibres

Søren Barsberg<sup>1</sup>, Jens Hassingboe<sup>2</sup>

<sup>1</sup> Plant Fibre Laboratory, The Royal Veterinary and Agricultural University, Højbakkegård Allé 1, DK-2630 Tåstrup, Denmark, sbar@kvl.dk

<sup>2</sup> Jens Hassingboe, Coloplast A/S, Bakkegårdsvej 406A, DK-3050 Humlebæk, Denmark, dkjhb@coloplast.com

**Keywords:** Laccase, lignin, oxidation mechanisms, fibreboard, TMP

### ABSTRACT

In the MDF fibreboard industry, environmentally unsafe adhesives are added to the fibres in order to produce hot-pressed boards of sufficient strength. Several research groups have demonstrated that the enzyme laccase can be applied in a pre-treatment of the fibres, which enhances their autoadhesion considerably. This promises the replacement of adhesives with a safe and mild enzymatic treatment. The laccase treatment does, however, not always produce an acceptable autoadhesion enhancement. In the present work, it is examined whether the effect of laccase on board strength is independent of the addition of wax to the fibres. In spite of the use of a relatively high laccase dose for the fibre treatment the autoadhesion enhancement is weak. Wax addition causes a slight reduction of board strength, which appears to be independent of the laccase treatment. The basic chemical-physical mechanisms of the laccase catalysed strength enhancement are discussed, and it is concluded that they are not well understood. More research is necessary in order to obtain a more robust and predictable effect of laccase, which does not depend on a “lucky” choice of fibres.

### INTRODUCTION

The enzyme laccase catalyses the oxidation of a broad range of substrates, such as phenols, and transforms thereby oxygen to water (Mayer and Staples 2002). Laccase may be utilised to produce lignin oxidation products derived from lignin phenolic groups in wood pulps. Subsequently, the pulp can be used as raw material for producing adhesive-free hot-pressed boards due to the beneficial effect of these products. This concept has been examined by several research groups with the aim of replacing the environmentally unsafe adhesives used in the Medium Density Fibreboard (MDF) industry with a laccase pre-treatment of the pulp (Felby *et al.* 1997a, Felby *et al.* 2002, Unbehau *et al.* 2000, Huttermann *et al.* 2001, Kharazipour *et al.* 1998). The results have been promising.

An interesting issue, which has been largely neglected, is the fact that it does not always work. Negative results are seldom of interest and rarely published. We have experienced instances where the laccase treatment resulted in insufficient board properties, whereas in other cases good properties, similar to conventional adhesive-containing boards, were achieved. These differences are believed to arise from the use of different thermo mechanical pulp (TMP) batches. “Successful” batches were obtained when wood chips were pre-cooked for a few minutes longer than standard, before entering the disc refiner.

The resulting fibre properties depend of course on such pre-treatments. The pre-cooking affects all cell wall components, and for lignin it may induce various chemical reactions such as oxidation, condensation and bond cleavage. Prolonged pre-cooking produces a wood chip, which

is then relatively more modified. This will distinguish the result - *i.e.*, the chemical-physical state of a TMP fibre - of further reactions, which take place during disintegration of the chip in the refiner.

The state of a TMP fibre depends on this pre-history. A reasonable suggestion is that prolonged pre-cooking produces a larger amount of lignin oxidation products, such as quinone moieties. These may survive the refining, and may alter both the chemical properties of lignin, but - perhaps more important - also the macromolecular flexibility of the lignin polymer (*e.g.*,  $T_g$  - the glass "transition" temperature).

The laccase treatment modifies the surface lignin of the fibres. It generates lignin radicals, as well as products derived from these (Felby *et al.* 1997b, Barsberg and Thygesen 1999, Barsberg 2002). Some of the radicals are long-lived and may couple during hot pressing to cause increased autoadhesion. It cannot be excluded that other types of oxidation products may have a similar effect. Thus an increased autoadhesion may also arise from, *e.g.*, increased Lewis acid-base interactions due to generation of carbonyl products.

This lignin modification depends obviously on the chemical state of lignin (*e.g.*, redox properties of lignin) and may also depend on the physical state of lignin, such as its density. An important characteristic of the modification is the localisation of lignin radicals, since they may only be effective in enhancing the fibre-to-fibre bonding if located near the surface. The physical state of lignin may play a role for the localisation and stability of radicals. Thus the chemical-physical state of a TMP fibre determines both (1.) its ability to bond to other fibres, as well as (2.) the lignin modification resulting from a laccase treatment. It is likely that these two types of fibre properties are closely related or correlated.

This enzyme technology needs further development towards (further) enhanced fibre autoadhesion, increased moisture stability of boards, and *not the least* increased repeatability and robustness of the laccase treatment in relation to board properties. This aim does, however, require an improved basic understanding of the chemical-physical phenomena on which the technology relies.

In the present work we examine the effect of a laccase treatment on the autoadhesion of beech TMP. Compared to previous work a relatively high amount of enzyme was applied. The compatibility of this treatment with wax addition to the pulp prior to the treatment was also examined.

## EXPERIMENTAL METHODS

### *Materials*

Beech (*Fagus sylvatica*) TMP was supplied by the (now former) MDF board plant of Junckers Industries, Køge, Denmark, where it was produced by an Asplund process. The moist fibres were frozen after fibrillation. A fungal *Trametes villosa* laccase, SP504 (EC 1.10.3.2), was supplied by Novozymes A/S, Bagsværd, Denmark. The enzyme was contained in a carbohydrate solution with a specific activity of 440 U/ml, where 1 U is the amount of enzyme which oxidises 1  $\mu$ M/min syringaldazine (50 mM potassium buffer pH 5.5, 30°C). Wax (Mobilcer 138, 59% wax in aqueous emulsion) was supplied by Esso S. A. F., Exxon Mobil oil Corporation, European Technology Centre, France. Fluorescein was from Riedel-de Haën. Fluorescein was added to the wax suspension in  $10^{-4}$  M (*i.e.*, a relative mass fraction of  $6 \cdot 10^{-5}$ ) to produce a fluorescent wax

for future fluorescence microscopy studies of wax-fibre interactions. This fluorescent wax was used in the present work.

### ***Wax addition***

The fibres were dried to 90% dry matter content. The wax suspension was then added using a spray pistol fed by a pump at a well-defined rate. The fibres entered a tube system (a part of a DanWeb fibre mat-forming setup) in a well-defined feeding rate (g/s). The last part of the tube had a 90° bend ending in a 2 m long straight tube section. The pistol was mounted at this bend, such that the wax was sprayed into the middle of the tube (last part), parallel with the flow direction. The fibres were collected at the end of the tube. Fibre samples were produced containing 0, 0.5, 1 and 2% (by dry matter weight) wax.

### ***Laccase treatment***

Each fibre sample (1400 g) was suspended in 14 L de-ionised water and K Acetate buffer (1 M, pH 4.5, 0.14 L) was added to ensure an optimal pH for the enzyme activity. The pH of the fibre suspensions was 4.8 due to the buffer-effect of the fibres. The temperature was 20° C. The laccase treatment was initiated by addition of laccase solution (30 U pr. gram dry fibre mass). After 1 h, the suspension was centrifuged and the treated fibres dried. Control samples were produced by the same procedure, except that no laccase solution was added. Thus two (laccase) by four (wax) sample types were produced.

### ***Board production and -testing***

Airlaid fibre mats of 30 x 30 cm were formed and conditioned for 24 h at 90% RH. Four boards for each sample type were produced by hot pressing (200°C, 5 min, 70 bar: Target density 850 kg/m<sup>3</sup> and –thickness 3 mm). Each board was first cut such that the outermost 7 cm edge of all four sides was discarded. The inner 16 x 16 cm was cut into three strips of 5 x 16 cm defining one *middle strip* (containing the centre of the original whole board), and two *side strips* on each side of the middle strip. The board strips were conditioned at 65±5% RH, 20±2°C and tested to obtain the modulus of elasticity (MOE) and –rupture (MOR) according to European Standard EN 310:1993.

## **RESULTS AND DISCUSSION**

### ***Results***

For each sample type four boards were produced, *i.e.*, four middle strips and eight side strips. In table 1 is shown the average  $\rho_s$  (of eight) of the side strip densities in *units* of the average (of four) of the middle strip densities. Thus an ideal homogeneous board has  $\rho_s = 1$  by definition. Edge effects, *i.e.*, a side strip positioned too close to the original board edge, should affect the density of the side strip such that  $\rho_s < 1$ .

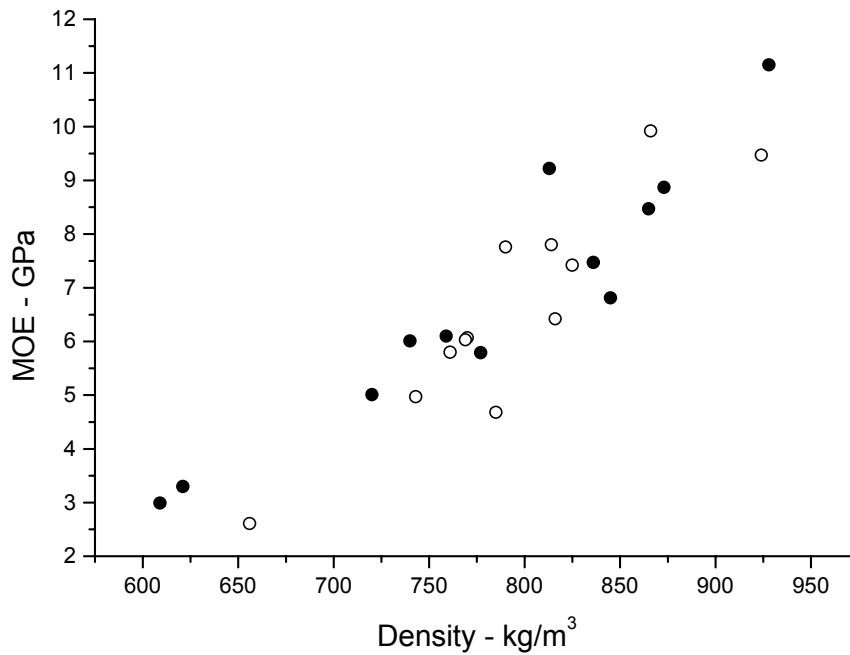
***Table 1: Density homogeneity parameter  $\rho_s$  for all sample types The density homogeneity parameter. “C” is a control sample, “L” a laccase treatment sample, and the percentage value denotes wax content. The errors are estimated from the standard deviation of the average through error propagation.***

C-0%: 0.95±0.04	C-1/2%: 1.02±0.06	C-1%: 0.96±0.04	C-2%: 0.94±0.03
L-0%: 0.94±0.07	L-1/2%: 0.99±0.06	L-1%: 0.96±0.04	L-2%: 0.93±0.03

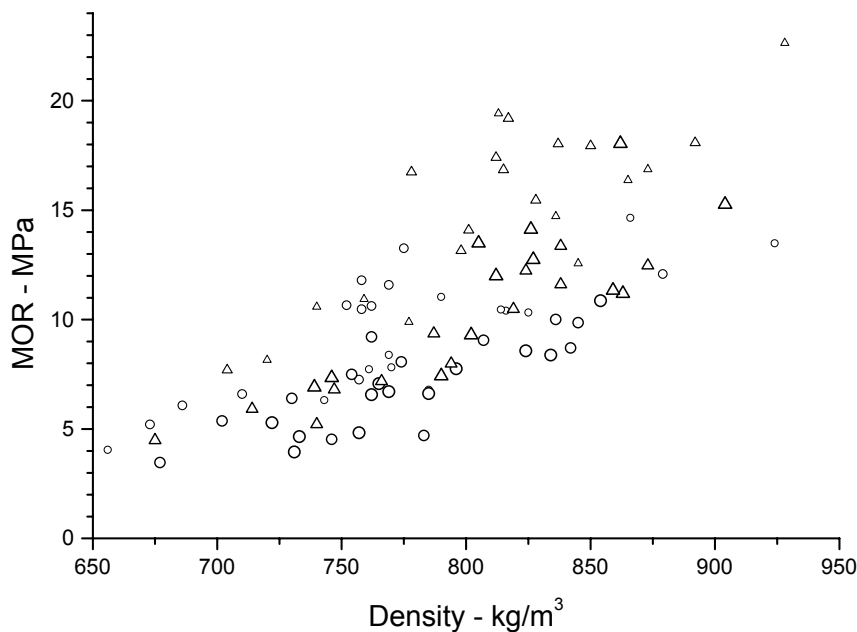
The  $\rho_s$  values suggest that the boards have reasonable homogeneity within the 16 x 16 cm test area. Therefore we report the results such that the side- and middle strips are treated on an equal footing. Each sample type is thus represented by twelve values of MOE, MOR and density.



In Fig. 1 is shown the MOE for the 0% wax sample types. There is a clear general increase of MOE with board density. There is, however, no difference between the control and the laccase treated sample.



*Figure 1: Strips from enzyme treated boards are closed circles and strips from control boards are open circles.*



*Figure 2: Strips from enzyme treated boards are up-triangle symbols and strips from control boards are circles. Wax content correlates with symbol size: 0 % wax is represented by smallest symbols, and 2 % with largest symbols.*

Although the MOR results, depicted in fig. 2, show that the boards are generally of weak strength, the control and the laccase treated samples are distinguished at densities  $>800 \text{ kg/m}^3$ , where the laccase treated samples show a relatively small increase of strength. For both

treatments the wax pre-treatment causes a strength reduction. Comparison of the two sample types with 2% wax suggests that the presence of wax on the fibres does not neutralise the effect of the laccase treatment. As for MOE there is a clear general increase of MOR with board density. Inspection of Fig. 2 also suggests that the laccase treatment has a slight densifying impact on the boards, whereas the wax treatment has not.

A classification of all samples into a control group C and a laccase group L (each of which contains 48 strips/values including all wax treatments) yields mean densities of  $\rho_C = 769 \pm 9 \text{ kg/m}^3$  and  $\rho_L = 794 \pm 11 \text{ kg/m}^3$ , respectively. The uncertainty is estimated as the standard deviation of the mean. If all samples are classified into a low-wax LW (0 and 0.5% wax) and high-wax HW (1 and 2% wax) group, the mean densities are  $\rho_{LW} = 775 \pm 12 \text{ kg/m}^3$  and  $\rho_{HW} = 788 \pm 8 \text{ kg/m}^3$ , respectively. A division of all samples into two groups, which should *a priori* not differ, is achieved by mix group 1 – containing *one half* of the four boards of *all* sample types – and mix group 2, containing the remaining half. The mean densities of these are  $\rho_1 = 785 \pm 10 \text{ kg/m}^3$  and  $\rho_2 = 779 \pm 10 \text{ kg/m}^3$ . The statistical significance of the observed densifying impact of the laccase treatment is thus suggested.

## DISCUSSION

Fig. 2 shows that density is an indispensable parameter in relation to laccase-catalysed (LC) autoadhesion. In order for the treatment to be beneficial for fibre-to-fibre bonding, a close molecular association of surface lignin of the fibres must necessarily occur. This ensures covalent coupling of the long-lived radicals, or non-covalent inter-molecular interaction between the modified fibre surfaces, or a combination of both. In order for such interactions to be effective in improving board properties, a sufficient fibre-to-fibre average area  $A$  of contact must also exist. The criteria of sufficient contact area relates (in a purely geometrical way) to density.

The strength of bonding achieved within  $A$  may be expressed as an interfacial free energy of association  $\gamma_{12}$ , *i.e.*, the work pr. unit area required to separate two bonded fibres. This interfacial energy is caused by inter-molecular interactions and is thus their macroscopic expression. Chemical modification of the fibre surfaces causes modifications of inter-molecular interaction. Thus we may define  $\gamma_{12} = \gamma_{12}^0$  of non-modified, and  $\gamma_{12} = \gamma_{12}^0 + \Delta\gamma_{12}$  of modified fibre surfaces. Assuming an unaltered  $A$ , the catalytic effect of a chemical treatment – such as the laccase treatment – on inter-fibre bonding is expressed through  $\Delta\gamma_{12}$ .

Physical phenomena determine in a complex way – in conjunction with surface chemistry – the final properties of the boards (Bolton and Humphrey 1988, Carvalho and Costa 1998). The relatively large strength variation of all samples is in part due to density variation, which may be caused by vapour pressure variation due to moisture content variations of the fibres. The fibre surfaces are chemically modified during hot pressing by heat, mechanical pressure and vapour- and oxygen pressure. It is also well known that the molecular flexibility of lignin – expressed by  $T_g$  – depends on vapour pressure, hence the moisture content of the fibres (implicitly neglecting any occurrence of chemical modifications during this thermodynamic change-of-state). Thus moisture content variations will for these reasons cause variations of  $\gamma_{12}^0$ .

Small values of  $\gamma_{12}^0$  – *i.e.*, weak microscopic bonding – may give rise to a geometrical “spring-back” effect of the board, reducing its density. The overall bonding, *i.e.*,  $\sim \gamma_{12}^0 A$ , is then insufficient and results in a relatively large decrease of  $A$  upon release of pressure. It is also likely that fibre cell wall modifications, affecting both the surface, *e.g.*,  $\gamma_{12}$ , as well as the interior of the cell wall, will affect the elastic properties of the cell wall, and thus  $A$ .

For these reasons  $\gamma_{12}^0$  and  $A$  are not independent parameters.

For a qualitative investigation of board strength we may substitute  $A$  for density. The dependence of strength  $S \sim \gamma_{12}A$  on density is clearly depicted in Fig.2 in terms of bending strength. This is expressed by the change of  $S$  with respect to  $A$ :

$$\frac{\partial}{\partial A} S = \frac{\partial}{\partial A} (\gamma_{12}A) = A \frac{\partial}{\partial A} \gamma_{12}^0 + A \frac{\partial}{\partial A} \Delta\gamma_{12} + \gamma_{12}^0 + \Delta\gamma_{12} \quad (1)$$

The last two terms represent the properties of an interface, which are independent of  $A$ , whereas the first two terms represent a change of interfacial properties  $\gamma_{12}$  with a change in  $A$ .

According to Eq. 1 a difference in strength (e.g., MOR) of equal-density laccase-treated fibre boards and control boards should lead to a difference in their strength-density functional behaviour. This is suggested by the data in fig. 2, since the MOR of the laccase treated samples are distinguished from the control for densities  $>800 \text{ kg/m}^3$ . More data for the high-density region could lend this further support, and could also address the question of whether the positive impact of the laccase treatment on board strength is highly density dependent? A confirmative answer to this question would imply that the two terms in Eq. 1 containing  $\Delta\gamma_{12}$  are relatively dominant for high densities ( $\sim A$ ).

The missing ability of the present work to present LC strength enhancements of similar magnitude, as reported in other works (Felby *et al.* 1997a): MOR increase from  $\sim 27$  to  $\sim 42$  Mpa, densities  $850\text{-}900 \text{ kg/m}^3$ , (Felby *et al.* 2002): MOR increase to  $\sim 46$  Mpa, densities  $820\text{-}870 \text{ kg/m}^3$ ), points to the fact that more knowledge on the molecular causes – expressed by  $\Delta\gamma_{12}$  – of this enhancement is desirable. Note that in the present work a higher laccase dose, compared to these other works, was used under nearly the same conditions. As noted above the presence of wax decreases the strength of all boards, but it is not known whether this decrease would be insignificant compared to a *more* effective laccase treatment, *i.e.*, whether the LC strength enhancement is independent of the presence of wax.

The fact that the MOR values of the control samples are approximately *half* of those control sample values reported in other works – compared at the same densities – suggests a relationship between  $\Delta\gamma_{12}$  and  $\gamma_{12}^0$ . Thus a *prerequisite* for a relatively large LC strength enhancement  $\Delta\gamma_{12}$  may be that the achievable degree of inter-fibre molecular association must already be high, as expressed by a high  $\gamma_{12}^0$  value, such that the beneficial effect of the LC surface lignin modification is enabled.

The commonly accepted opinion is that this effect is caused by long-lived lignin radicals, which polymerise during hot pressing of the fibres into boards. Such polymerisation has been demonstrated, although it is not known whether it occurs internally in colloidal lignin particles, or whether it actually occurs inter-fibre wise (Felby *et al.* 2002). It has, however, also been demonstrated that these long-lived radicals accounts only for a *minor* fraction of the total oxidation, *i.e.*, oxygen consumption (Felby 1997).

The TMP fibre modification achieved by the laccase treatment has also been examined by various spectroscopic methods. The oxidation products *derived* from radicals have been shown to lead to fluorescence quenching of the fibres (Barsberg and Thygesen 1999, Barsberg 2002). These non-radical products (possibly carbonyl products) may play an equally important role for the autoadhesion enhancement. They may lower the  $T_g$  of lignin, ensuring an increased

molecular contact during hot pressing, and they may increase Lewis acid-base interactions of the interface between fibres.

The LC oxidation is, however, not limited to the fibres since a major fraction of the total oxygen consumption is due to solubilised extractives. Some of these may function as redox mediators between the enzyme and the fibre surface (Felby 1997, Felby *et al.* 1997b). Furthermore, an oxidation product derived from an extractive compound may have different solubility compared to the parent compound and may thus precipitate on a fibre surface. Conversely, the production of oxidation products in surface lignin may also alter the solubility of low molecular weight compounds adsorbed to surface lignin, which may then migrate into solution. It is thus *not* possible to distinguish sharply between the fibres and the suspension, in which they are immersed during laccase treatment.

A suggestion for future work would therefore be to examine the relative importance of radical and non-radical oxidation products for the LC autoadhesion enhancement. It would also be desirable to examine the dependency of this enhancement on the chemical-physical state of the fibres *prior* to the enzyme treatment. This state could also be manipulated by laccase treatment or by other types of treatments.

## CONCLUSIONS

In accordance with previous work a pre-treatment of beech TMP fibres with laccase lead to enhancement of the fibre autoadhesion in adhesive-free hot pressed fibreboards. The enhancement only occurred for densities above a critical value of  $\sim 800 \text{ kg/m}^3$ , and for these densities it was considerably smaller than previously reported. Addition of wax to the dry fibres after the pre-treatment and before pressing did not affect this strength enhancement, but led to a slight and even strength reduction of all boards. It is not known whether a larger strength enhancement would still be independent of the presence of wax. Board density is an important parameter and strength measures should be depicted as function of density. The laccase treatment has a weak densifying effect on fibreboards, which may be relatively larger for a more "effective" treatment. Board density and (changes in) fibre interfacial physics/-chemistry are interrelated. The degree of LC autoadhesion enhancement is suggested to depend on the autoadhesion strength, which can be obtained with control fibres. The chemistry and physics behind LC autoadhesion is highly complex and to this date not much explored.

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## Treatability of Refractory Wood Species after Fungal Pre-treatment

K. Messner<sup>1</sup>, A. Bruce<sup>2</sup>, H.P.M. Bongers<sup>3</sup>

<sup>1</sup> LIGNOCELL Holz-Biotechnologie, A-1170 Wien, Neuwaldeggerstrasse 16/3/7, lignocell@aon.at

<sup>2</sup> University of Abertay, Dundee, a.bruce@abertay.ac.uk

<sup>3</sup> SHR Timber Research, PO Box 497, 6700 AL, Wageningen, the Netherlands, f.bongers@shr.nl

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### ABSTRACT

The permeability of many wood species including Douglas fir, Norway spruce, Sitka spruce and fir can be reduced to 1-5% of that of green timber when dried, resulting in a radial penetration of chemical solutions of only a few millimetres. Exploitation of these wood species is not therefore possible for applications where full sapwood impregnation is needed. Additionally, 6 mm lateral penetration into exposed heartwood is required for sawn wood in ground contact. Pit closure upon drying is considered to be the reason for loss of penetrability / permeability. The main technologies currently in use to overcome the problem of pit closure are oscillating pressure methods and incising. A novel patented biotechnological method to make refractory wood species treatable, based on the pre-treatment of wood with fungi selected from a wide array of strains, has been developed by LIGNOCELL Wood-Biotechnology GmbH (Austria) and the University of Abertay (Dundee, Scotland). Scaling-up of the pre-treatment method for round wood led to a very simple and successful process, based on spraying the wood with a suspension of fungal spores in a nutrient solution onto non-decontaminated wood. It is also shown in this paper that the method can be extended to heartwood when certain strains of Basidiomycetes are used for pre-treatment, which will broaden the field of application of this technology. One very promising result is the pre-treatment effect achieved after acetylation of spruce heartwood. It shows that the pre-treatment method is not only restricted to wood preservatives but can also be used in combination with modern methods to improve the properties of wood. The key to success when using the pre-treatment method is the use of selected fungal strains together with a cheap nutrient solution. The advantage of using fungi compared to enzymes to improve penetrability is that these organisms can be sprayed as relatively cheap spore suspension onto the wood and will act as production and transport system of a broad mixture of enzymes into the wood leading to prevention of pit closure.

### INTRODUCTION

#### *Use of refractory wood species*

Many processes aiming at improved wood properties, including wood preservation, fire protection, improving dimensional stability or hardness, involve pressure treatment to achieve satisfactory penetration of chemicals into wood. The permeability of many wood species including Douglas fir, Norway spruce, Sitka spruce and fir can be reduced to 1-5% of that of green timber when dried, resulting in radial penetration of liquids of only a few millimetres. For use of wood in ground contact as well as non-ground-contact applications, exploitation of these wood species is largely restricted to applications where sapwood impregnation is not essential. According to EN 355-1, for commodities in Hazard Class 3, like external joinery such as windows, doors *etc.* minimum 6 mm lateral and 50 mm axial penetration of the preservative is

required. Full sapwood penetration is required for external cladding or garden timbers and especially for uses in Hazard Class 4, such as round wood in ground contact. For sawn wood in ground contact, an additional 6 mm lateral penetration into exposed heartwood is required. Standards for chemically modified wood (*i.e.* acetylation, resins, oils) do not exist at the moment but in order to be successful, impregnation of the modifying chemical needs to be complete.

### ***Wood structure and pits***

In softwood, liquids flow in the radial direction as well as in the longitudinal direction along the tracheids. Various authors emphasised the importance of radial flow of wood preservatives, *via* ray parenchyma cells as well as ray tracheids (Liese and Bauch 1967, Comstock 1970) into longitudinal tracheids, in order to achieve full sapwood impregnation. It can be concluded that at least in wood of large dimensions, preservatives or other chemicals enter the sapwood of softwood primarily through this route. Radial penetration between longitudinal fibres is expected to be limited because pits are located mainly on the tangential side of the fibres and much less on the radial side.

The flow of chemicals is enabled and controlled by the different types of pit passages. In some wood species, closed pits are the limiting factor for impregnation. Although the anatomical structure of pits can be very different, depending on the wood species and the connecting cell types, all types of pits consist of a pit membrane derived from the middle lamella of the cell wall sandwiched by the two adjacent primary walls. In softwood, the pits linking two tracheids are bordered, while pits between ray parenchyma cells and either ray tracheids or longitudinal tracheids are only half bordered at the tracheid side. Ray parenchyma cells are linked by simple pits lacking borders.

Pit membranes are considered to have the most significant influence on flow properties (Banks 1970). Bordered pits of coniferous wood become aspirated during drying. The torus is pressed against the porous, blocking the aperture and preventing the penetration of fluids. In some wood species including different types of spruce, this process is irreversible and even the sapwood becomes untreatable. One of the reasons might be hydrogen bonding between adjacent cellulose chains but other gluing reactions including resinous compounds may also play a role. The same aspiration process happens during heartwood formation but in addition the closed pit membranes of heartwood become thickened by incrustations (Coté 1963) including compounds such as lignans (Fengel and Wegener 1984).

The thickness of the pit membrane is an important dimension affecting flow resistance (Siau 1984). The membranes of softwood ray cells consisting of the primary cell wall are much thicker than the tori of bordered pits (Desch and Dinwoodie 1996), nevertheless they are considered to be the predominant radial passage for chemical solutions into wood during impregnation. Especially in simple pits and half bordered pits of wood rays where fats, waxes, fatty acids, and other extractives and storage materials contained in parenchyma cells may be involved in sealing the membranes of these pits when wood is dried. However, the true chemical reactions of pit closure are still speculative.

The main technologies currently in use to overcome the problem of pit closure are oscillating pressure methods and incising. After 15-20 hours oscillating pressure treatment of spruce or fir poles with CCB, a copper penetration of 22 mm can be achieved (Graf and Bör 1999). Incising is more commonly used for sawn wood (Morris *et al.* 1994). Penetration of CCA has been reported up to 10-15 mm at an incision depth of 5 mm and an incision density of 7300 per m<sup>2</sup> (Anderson *et al.* 1995). Zahora and Hösli (1997) reported achievement of CSA and AWPA requirements for in ground use of Black spruce lumber after incising at a density of 9500 per m<sup>2</sup> and 4.5 h

treatment. Although both methods can be applied to an extent where requirements for certain applications can be reached, methods leading to lower operating costs and increased qualities of treated wood would be of advantage for the wood preservation industry.

An old practice was to use the potential of micro-organisms for impregnability improvement of wood by storing logs in water where the wood was colonised by bacteria, attacking the pit membranes. However, the results were very inconsistent. Positive effects on permeability by wood treatment with a mixture of cellulases and hemicellulases were reported by Nicholas and Thomas (1986) and Militz (1993a, b). However, the improvement was not sufficient to allow the development of a reproducible technical process, probably due to the complex mechanism of pit closure. With a much broader spectrum of enzymes, however, the permeability might be improved considerably.

Some selected fungi adapted to grow on wood and to some extent also bacteria may provide the required broad enzyme spectrum. Fungi are best qualified for the purpose, as they actively grow into wood by hyphae and excrete their enzymes on site. The main routes of invasion for fungi are the wood rays where nutrients, stored in parenchyma cells are easily available (Eriksson *et al.* 1990). From the rays, the hyphae can move into the longitudinal tracheids via the pits. By excreting their enzyme systems they alter the chemistry and structure of pit membranes. This effect is most pronounced in the wood rays, where intensive fungal growth can be observed in the early stages of colonisation. Some fungi were found to extensively decompose the content of parenchyma cells, including lipophilic compounds (Fischer and Messner 1994) and this can be assumed to improve radial penetration of chemical solutions. Such enzymes may also be involved in cleavage of any compounds that are sealing the simple and half bordered pits, as well as the pits of longitudinal tracheids, thereby allowing the flow of liquids even after wood drying.

#### ***Fungal pre-treatment***

A novel biotechnological method based on the pre-treatment of wood with fungi carefully selected from a wide array of strains has been proven to considerably improve the permeability of refractory wood to subsequent chemical treatments. It has been developed in a joint effort by LIGNOCELL Wood-Biotechnology GmbH (Austria) and the University of Abertay (Dundee, Scotland) and was patented (Messner *et al.* 1999). It improves permeability of refractory wood species considerably (Rosner *et al.* 1998, Tucker *et al.* 1998). Two types of fungi, i) either wood colonising moulds like specific strains of *Trichoderma* or ii) weakly wood degrading basidiomycetes were chosen for enhancement of the permeability. The pre-treatment process includes inoculation of wood with fungal inoculum containing a nutrient solution and subsequent incubation. When using weak wood degrading basidiomycetes, prior decontamination of the wood surface by short steaming is recommended. Furthermore, eradication of the fungi by subsequent heat treatment is required. After incubation for 4 weeks with *Trichoderma*, or 1 week with basidiomycetes and subsequent pressure treatment with creosote GX+ in a conventional Rueping process, full sapwood penetration of spruce logs was achieved (Rosner *et al.* 1998, Tucker *et al.* 1998).

This paper reports on a further optimisation and scaling-up of the fungal pre-treatment process for wood preservation and its application for acetylation of wood. Furthermore, we report that heartwood of spruce may also be treatable by this process.

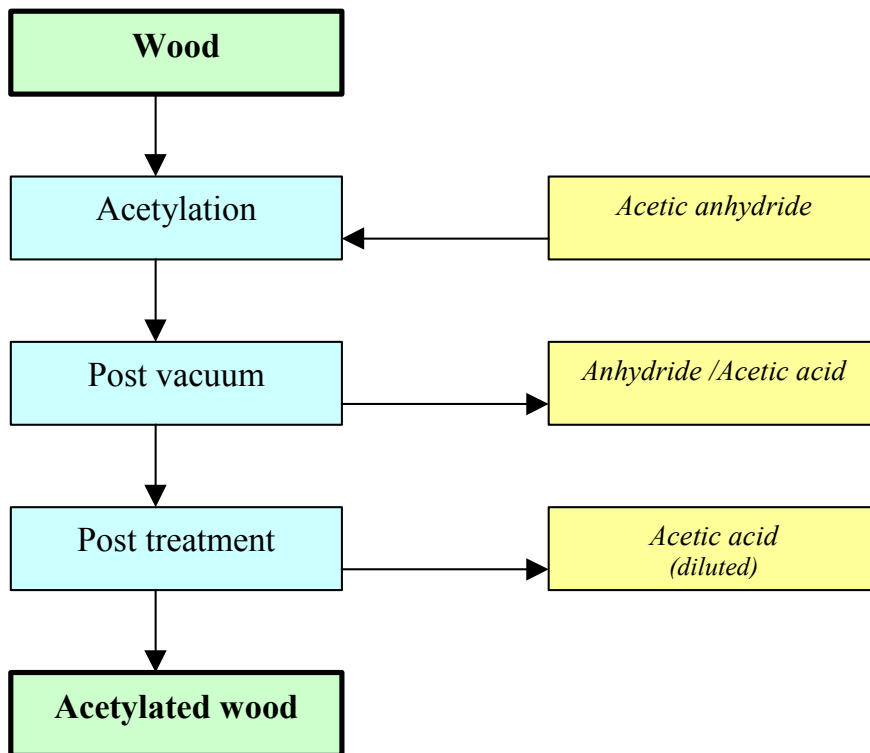
#### ***Acetylation***

The acetylation of wood with uncatalysed acetic anhydride has been studied extensively and shown to be one of the most promising methods for improvement of the technical properties of wood products. Especially the durability and dimensional stability is increased by this chemical



modification method. (Beckers 1998, Beckers *et al.* 1998, Beckers and Militz 1994, Beckers *et al.* 1994, Goldstein *et al.* 1961, Larsson and Simonson 1994, Larsson-Brelid *et al.* 2000, Militz 1991, Rowell *et al.* 1989, Singh *et al.* 1992).

In order to be acetylated, the cell wall material needs to be in intimate contact with the acetylation agent (acetic anhydride). The crucial part of the acetylation process therefore is the impregnation step before acetylation (figure 1). Refractory (difficult to impregnate) wood species, like spruce and Douglas fir, are therefore not generally suitable for the acetylation process where large dimensions are to be used and a complete (through and through) treatment is required. Methods to improve the impregnability of a wood species, such as fungal pre-treatment, could therefore be a solution to upgrade refractory wood species and allow them to be treated by acetylation.



*Figure 1: Steps in the acetylation process*

## MATERIALS AND METHODS

### *Fungi*

After careful screening of an extensive range of fungal species special strains demonstrating a high activity to improve preservative penetration in spruce were selected and patented (Messner *et al.* 1999). These strains belonged either to the genus *Trichoderma* or to *Basidiomycetes* exhibiting a very moderate effect on the wood cell walls within the first two weeks of incubation. Besides selected sporulating green cultures of *T. harzianum*, *T. viride* and *T. aureoviride*, a sporulating white strain and a non-sporulating strain of *T. harzianum* are generally used for our pre-treatment experiments. For heartwood pre-treatment *Dichomitus squalens* LC6 and *Phanerochaete chrysosporium* LC5, have produced satisfactory results and were included in the experiments reported here.

### *Scale up of fungal pre-treatment for Norway and Sitka spruce distribution poles and logs*

The efficiency of the fungal pre-treatment method to make spruce logs treatable was demonstrated on laboratory scale in prior experiments (Rosner *et al.* 1998, Tucker *et al.* 1998). These experiments were followed by the development of a pilot treatment plant for the pre-treatment of commercial timbers including distribution poles (Martin 2000). The plant (figure 2) was used to treat full sized Norway and Sitka spruce distribution poles as well as shorter (3 metre long) logs with *T. aureoviride*. Operation of the pilot plant process included steam sterilisation of the timber followed by spraying of the fungal inoculum in a nutrient base while poles/logs were slowly pulled through the plant at approximately 2 m/min. The timber was then incubated at ambient temperature prior to drying and commercial creosote treatment using standard industrial processes. Although the treatment plant operated very successfully and processed the poles in quick time the results were variable. Although some logs showed excellent increases in penetration of creosote (*T. aureoviride* pre-treated Sitka spruce – 26 mm compared with controls – 2 mm) others were less effective.

A second experiment was therefore set up to establish the critical parameters necessary for successful fungal pre-treatment. Sixty five logs (55 Norway spruce and 10 Sitka spruce) approximately (650mm x 20mm dia.) were debarked shortly after felling and were split into groups of five replicates to determine the effect of timber moisture, nutrients, incubation temp and steam treatment on *Trichoderma* colonisation. All logs were debarked immediately before being sterilised prior to *Trichoderma* treatment, except for ten which were allowed to air dry to either 100% or 50% moisture content before being sterilised and treated with *Trichoderma* spores. The majority of the logs for *Trichoderma* treatment were autoclave sterilised, except for ten that were surface sterilised by steam washing for approximately 10 seconds at high (180<sup>0</sup>C) or medium (120<sup>0</sup>C) steam temperatures in the pilot treatment plant. Five others were left unsterilised. All treatments except controls were subjected to *Trichoderma* treatment by rolling the logs for a few minutes in a spore suspension of 10<sup>6</sup> spores/ml made up in the appropriate nutrient solution (two separate nutrient types were evaluated) in an autoclave bag. *Trichoderma* treated logs were then incubated at either 7<sup>0</sup>C, 16<sup>0</sup>C, 22<sup>0</sup>C or under ambient conditions (6-16<sup>0</sup>C) over a period of 4 weeks.

Controls were dipped for 30 seconds in a 0.25% solution of Hicksons Anti-blue anti-sapsatin chemical treatment but were not treated with *Trichoderma*.

After incubation, all logs including controls were air dried outdoors over a two-month period until they reached moisture contents below fibre saturation point. They were then end-sealed with epoxy resin before being pressure impregnated with creosote in a commercial treatment plant by using an empty-cell (Rüping) process. After treatment, logs were cut in half and preservative penetration measured before samples were excised and the creosote extracted and analysed to determine the appropriate creosote loadings within the treated timber.



**Fig.2: Pilot pre-treatment plant; poles/logs are drawn through the plant while being steam sterilised and inoculated.**

#### ***Fungal pre-treatment of spruce heartwood for CCB impregnation***

Five samples of unsteamed and steamed green sapwood and heartwood of Norway spruce (*Picea abies* (L.) Karst) of 3 x 3 x 60 cm were inoculated by dipping into nutrient solutions containing spores and/or mycelial fragments of the test fungi *Dichomitus squalens* LC6 and *Phanerochaete chrysosporium* LC5. After incubation for 2 weeks, the wood was steamed to eradicate the mycelium of the fungi growing in the wood, dried at 70°C to a moisture content of approximately 25% and pressure impregnated with CCB in a commercial treatment plant together with other wood material. To evaluate the depth of penetration, the wood samples were cross sectioned in the middle and penetration of copper was measured after contrasting.

#### ***Fungal pre-treatment of spruce sapwood and heartwood for acetylation***

Sapwood and heartwood of Norway spruce (*Picea abies* (L.) Karst) were pre-treated with *T. harzianum* LC1, *Dichomitus squalens* LC5, and a strain of *Chrysosporium* sp., respectively, according to the method described above for CCB treatment. The wood was dried and acetylated by SHR Timber Research in the Netherlands on pilot plant scale. The degree of acetylation (acetyl content) from one sample per category was determined by FTIR-ATR. FTIR-ATR is used to give an indication of the acetyl content (Beckers *et al.* 2002).

## RESULTS AND DISCUSSION

### *Scaling up of fungal pre-treatment of spruce logs*

The effect of decontamination by steaming, the effect of incubation temperature and the effect of initial moisture content of the logs were evaluated in a scaling-up experiment using *Trichoderma aureoviride* after 4 weeks incubation time (table 1-3).

*Table 1: Effect of decontamination of logs by steaming on subsequent penetration of creosote:*

<b>Pre-treatment</b>	<b>Penetration (mm / No. of logs)</b>
Norway spruce	
Control	2.4 ± 1 / 5
Autoclave sterilisation	27.3 ± 4.8 / 5
High temp steam treatment	21.7 ± 5.5 / 5
Low temp steam treatment	22.7 ± 5.2 / 5
No sterilisation	24.6 ± 5.7 / 5
Sitka spruce	
Control	1.4 ± 0.7 / 5
Autoclave sterilisation	25.4 ± / 5

It is interesting to note that autoclaving or steam spraying using the pilot plant did not result in significantly greater creosote loadings in logs compared with those that were not surface sterilized. Full sapwood penetration was achieved without prior decontamination by steaming indicating that the *Trichoderma* was able to effectively colonise the timber in the face of competition from other transient colonisers.

*Table 2: Effect of incubation temperature of Norway Spruce logs on subsequent penetration of creosote:*

<b>Incubation temperature</b>	<b>Penetration (mm / No. of logs )</b>
Variable ambient temperature (6-16°C)	21.8 ± 6.0 / 5
22° C	27.3 ± 4.8 / 5
16° C	25 ± 4.9 / 5
7°C	24.8 ± 5.9 / 5

Full penetration of Norway spruce sapwood can be achieved at incubation temperatures of between 7- 22°C although slightly better penetration results were achieved at the higher temps.

*Table 3: Effect of starting moisture content of Norway Spruce logs on subsequent penetration of creosote:*

<b>Starting moisture content</b>	<b>Penetration (mm / No. of logs )</b>
Moisture content immediately after debarking (approx 200%)	27.3 ± 4.8 / 5
100%	27.5 ± 6.0 / 5
50%	14.5 ± 10 / 5

Impregnation of Norway spruce logs of different starting moisture contents indicates that this parameter more than the others tested has a very significant effect on subsequent colonisation and permeability enhancement by *T. aureoviride*. The depth of creosote penetration is very significantly reduced when moisture content drops down to 50% of the wood dry weight.



**Fig. 3: Sectioned logs of Norway spruce after fungal pre-treatment with *T. aureoviride*, incubation at ambient temperature, drying and subsequent and creosote treatment.**

The scaling-up experiment demonstrates that full sapwood penetration of Sitka and Norway spruce can be achieved across a broad temperature range when a suspension of the carefully selected strain *T. aureoviride* SIWT T1 in nutrients is used for inoculation provided the timber is still in a green state and has not dried out too much prior to fungal inoculation (figure 3). This factor is most likely to have been responsible for the variability of results recorded when full length poles were treated using the pilot plant as the pole material on that occasion had dried out somewhat during transportation and storage prior to *Trichoderma* inoculation. No further methods such as decontamination are needed making the method very simple and commercially attractive.

#### ***Fungal pre-treatment of spruce heartwood for CCB impregnation***

Figure shows the effect of pre-treatment of Norway spruce samples with two strains of Basidiomycetes compared to the non-pretreated control. *Phanerochaete chrysosporium* LC 5 is shown to improve penetration compared to the control, but it is much less effective than *Dichomitus squalens* LC6. Almost all of the steamed wood samples were completely penetrated by CCB. When steaming was omitted, some infections appeared on the wood surface, inhibiting slightly the growth of *D. squalens*, consequently resulting in reduced penetration of CCB (figure 4).

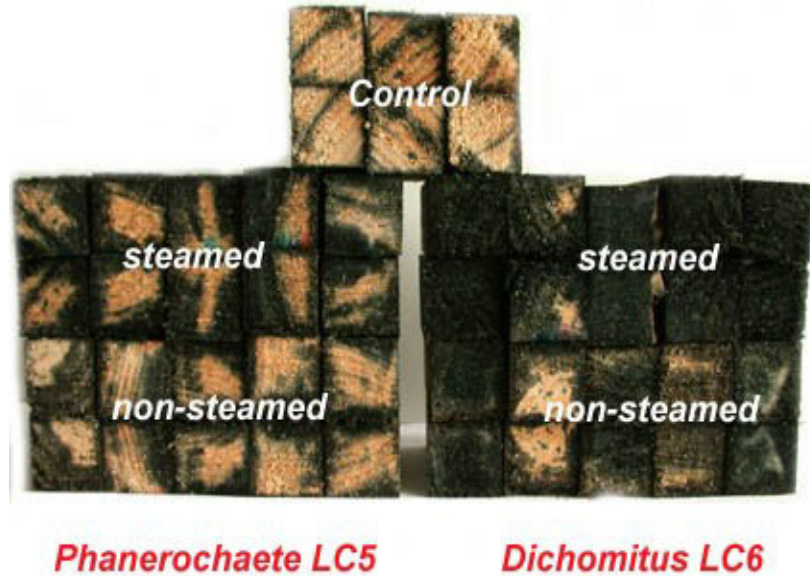


Fig. 4: Spruce heartwood pre-treated with Basidiomycetes and contrasted after impregnation with CCB

**Fungal pre-treatment of spruce sapwood and heartwood for acetylation**

In table 4 the acetyl content of the samples determined by FTIR-ATR are given for the sapwood and heartwood samples per type of fungal pre-treatment. All wood samples pre-treated with

Table 4: Acetyl content determined by FTIR-ATR for the sapwood and heartwood samples.

Gradient		Sapwood			
		0-2	2-5	5-10	10-rest
		[mm]	[mm]	[mm]	[mm]
Not acetylated	No pre-treatment	3.9	4.7	5.3	5.0
	<i>Chrysosporium sp.</i>	1.6	1.5	1.6	1.8
	<i>D. squalens</i> LC6	1.3	0.7	0.5	1.9
	<i>T. harzianum</i> LC1	2.4	2.1	1.6	4.1
Acetylated	No pre-treatment	20.0	22.4	17.1	19.1
	<i>Chrysosporium sp.</i>	20.3	18.9	16.2	16.9
	<i>D. squalens</i> LC6	16.2	15.3	15.8	16.0
	<i>T. harzianum</i> LC1	16.9	17.1	16.7	16.0

Gradient		Heartwood			
		0-2	2-5	5-10	10-rest
		[mm]	[mm]	[mm]	[mm]
Not acetylated	No pre-treatment	3.8	1.2	3.1	0.2
	<i>Chrysosporium sp.</i>				
	<i>D. squalens</i> LC6	1.7	1.6	1.3	0.7
	<i>T. harzianum</i> LC1				
Acetylated	No pre-treatment	16.8	15.9	11.8	7.9
	<i>Chrysosporium sp.</i>				
	<i>D. squalens</i> LC6	17.3	18.1	16.8	18.1
	<i>T. harzianum</i> LC1				

fungi have an acetyl content lower than that of the wood not colonised by fungi. Obviously, the fungi consume some of the acetyl groups present in native wood during growth. In general, the acetyl contents of the sapwood samples is of the same order for all pre-treatments.

However, when it comes to heartwood penetration, the acetyl content of acetylated spruce without pre-treatment rapidly decreases to almost the acetyl content of not acetylated wood with increasing depth. The wood pre-treated with *D. squalens* has a uniform acetyl content in depth, even below 10 mm depth. This result is in full agreement with the result achieved after CCB impregnation, demonstrating the ability of *D. squalens* to make heartwood of Norway spruce treatable.

The results shown in this paper confirm earlier results that pre-treatment of refractory wood species such as Norway spruce with selected fungal strains can lead to full sapwood penetration after pressure impregnation. Scaling-up of the pre-treatment method for round wood led to a very simple and successful process, based on spraying of wood with a suspension of fungal spores in a nutrient solution onto non-decontaminated wood. The key to success is the use of selected fungal strains together with a cheap nutrient solution. The method including fungal strains has been patented by LIGNOCELL Holz-Biotechnologie G.m.b.H and the University of Abertay (Dundee). Spore suspensions for pilot plant experiments are commercially available from the inventors of the process.

The effect of fungal pre-treatment is most probably primarily connected to the colonisation of wood rays and the depolymerisation of compounds contained in parenchyma cells as well as the enzymatic attack on the pits of ray cells, improving the radial flow of liquids and their penetration into the longitudinal tracheids.

It was also shown that the method can be extended to heartwood when certain strains of basidiomycetes are used for pre-treatment. This would allow the use of sawn spruce wood in soil contact where an additional 6mm penetration of heartwood is required. However, the experiments also showed that basidiomycetes are more sensitive to competing micro-organisms and decontamination by steaming improves the result. The advantage of using basidiomycetes like the selected strains of *Dichomitus squalens* or *Phanerochaete chrysosporium* instead of *Trichoderma* is the reduction of the incubation time to 1-2 weeks and the option to extend penetrability also to the heartwood area. However, prior decontamination of logs and subsequent eradication of the fungus has to be considered. If the incubation time is kept at 1-2 weeks, no or very little strength loss was measured in prior experiments. When using *Trichoderma*, the wood strength remains unchanged (Tucker *et al.* 1998).

The pre-treatment effect achieved after acetylation of spruce heartwood is particularly promising. It shows that the pre-treatment method is not only restricted to wood preservatives but can also be used in combination with chemical wood modification techniques to improve the properties of wood.

To date no experiments have been reported that can successfully improve penetration of refractory wood species to the same extent as that achieved with fungi. Since the mechanisms involved in pit closure are chemically complex it is clear that only a system that can deliver a complex mixture of different enzymes is likely to be successful. As enzymes cannot move into the wood on their own, their application would have to be linked to pressure treatment. The application of such an enzyme solution in a quantity needed for treatment cylinders can be considered commercially unfeasible. The advantage of using fungi compared to enzymes is that

these organisms can be sprayed as relatively cheap spore suspensions onto the wood and will act as production and transport system for a broad mixture of enzymes into the wood. The key for success is the use of the right fungal strains together with a cheap nutrient solution. Making heartwood treatable clearly requires basidiomycetes as these fungi also produce the ligninolytic enzymes necessary to dissolve lignin-like incrustations of pits in this material.

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**ENZYMATIC TREATMENTS**  
POSTER PRESENTATIONS



## Fungal Surface Modification of Soft Woods with the White Rot Basidiomycete *Ceriporiopsis subvermispora*

Karin Fackler<sup>1,3</sup>, Manfred Schwanninger<sup>2,3</sup>, Marjeta Sentjurc<sup>4</sup>, Miha Humar<sup>5</sup>,  
Crtomir Tavzes<sup>5</sup>, and Kurt Messner<sup>1</sup>

<sup>1</sup>Institute of Chemical Engineering, University of Technology Vienna, Getreidemarkt 9/ 166, A-1060 Wien, Austria, kfackler@mail.zserv.tuwien.ac.at

<sup>2</sup>Institute of Chemistry, BOKU - University of Natural Resources and Applied Life Sciences, Vienna, A-1190 Wien, Austria

<sup>3</sup>Competence Centre for Wood Composites and Wood Chemistry (Wood K Plus), Linz, Austria.

<sup>4</sup>Jozef Stefan Institut, Ljubljana, Slovenia

<sup>5</sup>University of Ljubljana, Biotechnical Faculty, Department of Wood Science and Technology, Ljubljana, Slovenia

**Keywords:** white rot, *Ceriporiopsis subvermispora*, infrared spectroscopy, electron paramagnetic resonance, phenoxy radicals

### ABSTRACT

Wood rotting basidiomycetes excrete a mixture of ligninolytic and hydrolytic enzymes and highly oxidative low molecular weight systems when they colonise wood. Their oxidative enzymes – mainly laccase – have been tested in the pulp, paper and board industry for delignification and surface activation of fibres. A biopulping process using the selective white rot fungus *Ceriporiopsis subvermispora* has been developed in order to reduce the energy requirement for thermomechanical pulp production. We tested several wood rotting fungi in short time fermentations, in order to modify the surface of softwood veneers and particles and focussed on the selective white rot fungus *C. subvermispora* which produces its ligninolytic system in the growth phase. It was shown by near infrared spectroscopy (NIR) that surface modification by fungi was achieved within a few days. In the same time range, stable free radicals were formed. FT-MIR spectra taken in later stages of decay showed that apart from delignification and hemicellulose degradation, carbonyl and/ or carboxyl groups were generated.

### INTRODUCTION

White rot fungi are the only organisms capable of mineralising the recalcitrant biopolymer lignin. This capability can be utilised also in industrial processes. Most of these fungi degrade lignin and wood polysaccharides more or less simultaneously, however in some cases (*Ceriporiopsis subvermispora*, *Dichomitus squalens*) lignin is mineralised selectively. This particular property has been used in the biopulping process: wood chips were incubated for several weeks with selective white rotters in order to reduce the refining energy in thermomechanical pulp production or to reduce the amount of cooking chemicals necessary for the production of chemical pulps (Akhtar *et al.* 2000, Messner *et al.* 1994).

However, it was not our intention to modify the whole wood matrix, but to utilise the oxidative enzymes and low molecular weight agents that are excreted by *C. subvermispora* to modify and activate the wood or fibre surfaces. The microbiologically modified wood may serve as raw material for products with novel properties.

Contrary to the model white rot fungus *Phanerochaete chrysosporium* that produces its lignolytic system under growth limiting conditions in later stages of cultivation, *C. subvermispora* modifies wood already in the growth phase (Rüttimann-Johnson *et al.* 1993). Thus, biotechnological applications are possible also in incipient stages of wood colonisation by this fungus.

Recently, we reported a darkening effect on the wood surface caused by *C. subvermispora*, which correlated with the ligninolytic enzyme production and a decrease of the surface lignin. Interior parts of the wood matrix were not visibly affected by the fungal treatment (Fackler *et al.* 2002a).

In this work, we focussed on the chemical changes of spruce wood including those of the surface. Wood samples were investigated by FT-IR in order to see changes of functional groups and to estimate the differences in lignin content of the wood surfaces.

## EXPERIMENTAL

### *Fungal Treatment of Spruce Veneers*

The fungal cultures (*Ceriporiopsis subvermispora* CBS 347.63) were pre-cultivated on malt extract agar (MEA) plates (Fluka). The spruce veneers (55 x 65 x 1 mm) were steam sterilised for 10 min at 121°C and soaked in 2% w/v corn steep liquor containing disintegrated fungal mycelium (1 MEA plate / 200 ml medium). The veneers were incubated for 5 or 10 days and 10 weeks at 30°C. After the fungal treatment, the mycelium was washed from the surfaces with distilled water, before drying the samples for 24 hours at 50°C. The dried samples were subjected to NIR, FT-MIR and wet chemical analysis (Schwanninger and Hinterstoisser 2002). EPR spectroscopy was carried out with moist samples.

### *NIR Spectroscopy of Wood Surfaces*

This was performed with a Bruker EQUINOX 55 spectrometer equipped with a fibre optic probe as described by Schwanninger and Hinterstoisser (2001). The relative lignin content was followed by comparison of the spectra in the 2nd derivative mode in the region from 6102 to 5762 cm<sup>-1</sup>, which is representative for lignin.

### *FT-MIR Spectroscopy of Wood Meal*

was performed with a Bruker EQUINOX 55 spectrometer in the middle infrared region using the KBr pellet technique. Therefore about 1.5 mg wood meal was mixed with 200 mg KBr and pressed to a pellet, from which a spectrum was recorded.

### *Electron Paramagnetic Resonance (EPR) Spectroscopy*

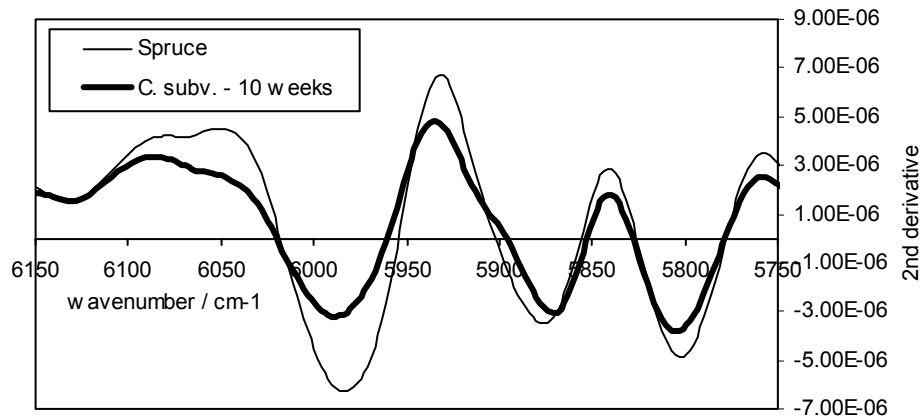
Spectra of moist samples (20mg) were recorded with a Bruker ESP-300 X-band EPR spectrometer. Microwave frequency was 9.62 GHz, microwave power 20 mW. Modulation frequency was 100 kHz, center field 340 mT, modulation amplitude 0.1 mT.

## RESULTS

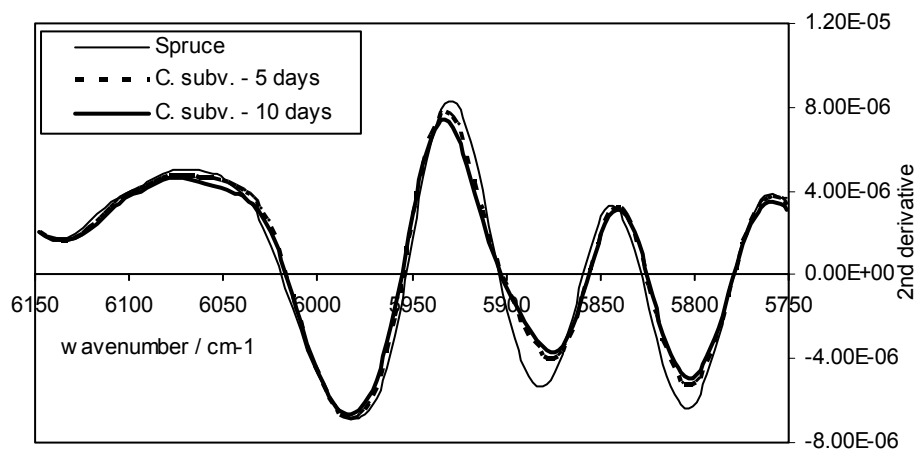
### *Infrared spectroscopy of wood meals and surfaces after colonisation with C. subvermispora*

Fig. 1 shows the NIR surface spectrum (2nd derivative mode) of *Ceriporiopsis* treated spruce wood veneer after 10 weeks incubation. The amplitude of the spectrum was much smaller, indicating a much lower lignin content of the sample as it was proved by wet chemical analysis: the Klason lignin determination was performed according to Schwanninger and Hinterstoisser (2002) and showed a decrease in total lignin content from 26.2 to 21.7% at an overall weight loss

of 24%, indicating that not only lignin, but also wood polysaccharides had been degraded. After only 5 and 10 days – the overall lignin content had not yet decreased (Fackler *et al.* 2002b) – the NIR measurements of the surface were already able to reveal a slight decrease of peaks in the same range of the NIR spectra at 5980, 5880, and 5800  $\text{cm}^{-1}$  (Fig. 2).



**Fig. 1.** NIR spectra in the 2nd derivative mode from the surface of untreated and 10 weeks with *C. subvermispora* incubated spruce veneers.



**Fig. 2.** NIR spectra in the 2nd derivative mode of spruce wood meal from untreated and 5 and 10 days with *C. subvermispora* incubated spruce veneer.

The FT-MIR spectra (Fig. 3) of wood meal samples showed the expected decrease of the lignin band at 1510  $\text{cm}^{-1}$  due to fungal treatment with the selective lignin degrader. Additionally, there is a remarkable increase at 1735  $\text{cm}^{-1}$  indicating a higher amount of non-conjugated ketones and aliphatic aldehydes or acetyl groups derived from hemicelluloses. However, the decrease of bands around 1250  $\text{cm}^{-1}$  shows that also high amounts of hemicelluloses were degraded by the fungus. Thus the increase of the C=O band is mainly caused by the oxidation of the lignin component. The relative increase of the absorption in the region of 1670 to 1650  $\text{cm}^{-1}$  is probably also caused by an increase of C=O stretching vibrations in conjugated p-substituted arylketones and carboxylic groups.



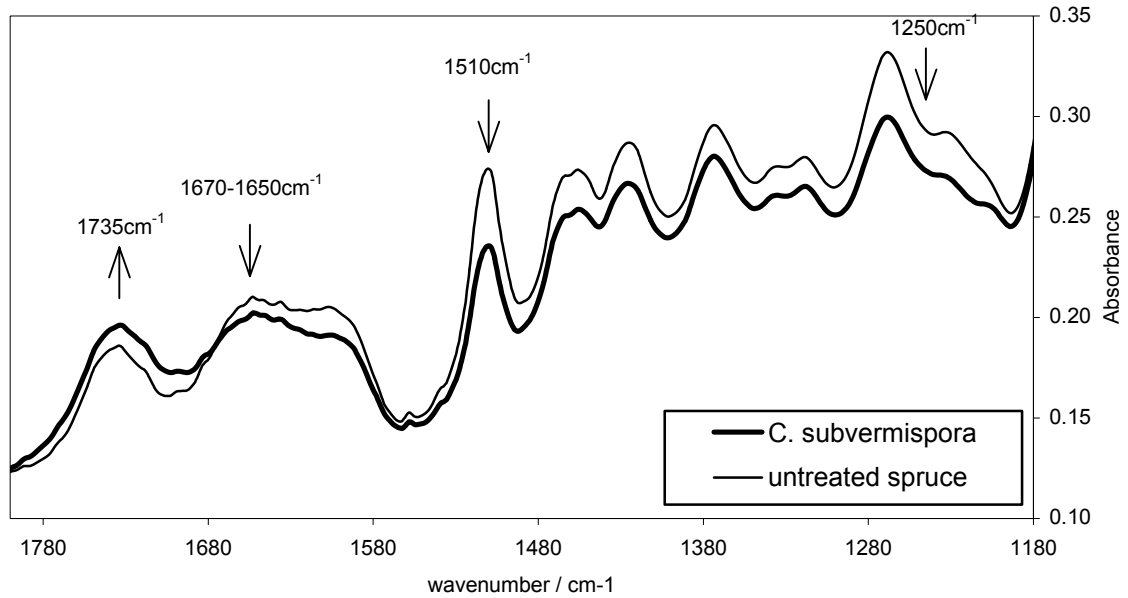


Fig. 3. FT-MIR spectra of untreated and 10 weeks *C. subvermispora* treated spruce.

#### ***Electron paramagnetic resonance spectroscopy of fungal treated spruce veneer***

A strong free radical signal was obtained after three days (not shown) and increased on the fifth day after inoculation of the spruce veneer (Fig. 4). The signal of *C. subvermispora* was very stable and originates most likely from phenoxy radicals bound to the lignocellulosic matrix. The signal is superposed by an Mn(II)-signal, which occurs also in the blank and is characteristic for moist wood. The radicals may be produced by phenoloxidase enzymes (e.g. laccase and manganese peroxidase) or by transition metal catalysed chemical reaction (Hammel *et al.* 2002; Messner *et al.* 2002). It is known that laccase forms stable free radicals on fibres and activates the lignin of fibre surfaces in order to increase their auto adhesive properties (Grönqvist *et al.*, 2002).

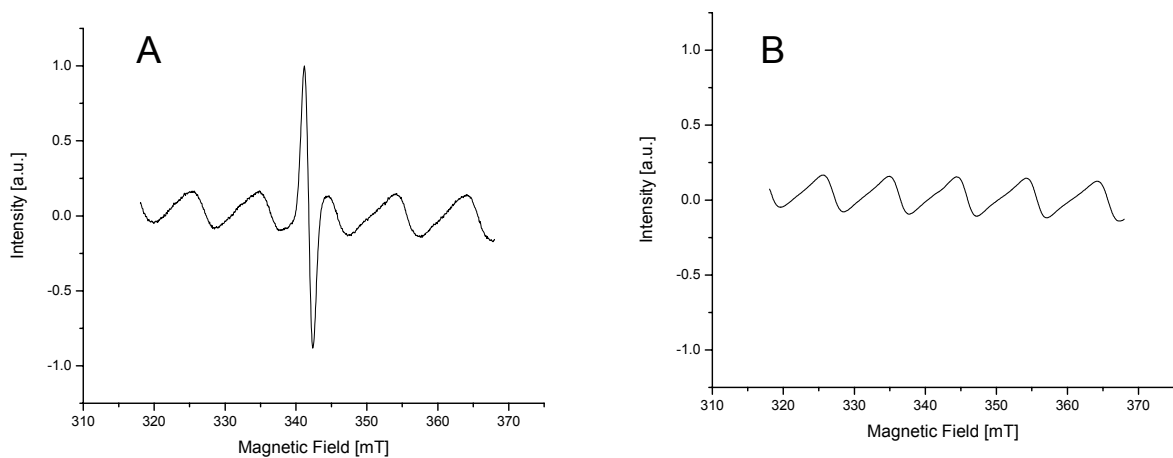


Fig.4. EPR signal after 5 days incubation with *C. subvermispora* (A) and untreated, moist control (B)

## CONCLUSIONS

The selective white rot fungus *Ceriporiopsis subvermispora* has great potential to modify and activate surfaces of wood and wood fibres within only a few days. The results of a five-day treatment were a lower surface lignin content and the formation of stable free radicals – probably phenoxy radicals immobilised on the wood matrix. Significant amounts of aldehyde and keto groups were formed and hemicelluloses content decreased during longer incubation times with the same fungus. It is likely that these chemical changes also start in earlier stages of colonisation. Due to the microbiologically generated new functional groups and / or the different distribution of the wood constituents on the surface, it is very likely that fungal modified wood got different properties compared to the raw material. Research concerning further details of chemical changes on the wood surfaces and their impact on the wood properties will be necessary in order to understand the mechanisms of wood modification by white rot fungi in the early stages of wood colonisation.

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## Lignocellulosic Composite Materials Bound by Natural Adhesives

R. Kozłowski, J. Batog, A. Przepiera

Institute of Natural Fibres, 60-630 Poznan, Wojska Polskiego 71b, Poland

E-mail: sekretar@inf.poznan.pl

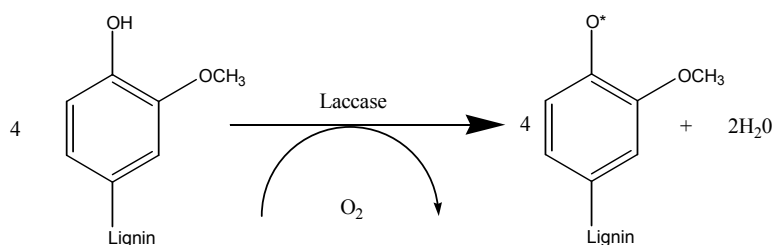
**Keywords:** lignocellulosic composites, enzymatic bonding, lignin, laccase

### ABSTRACT

Recently, research was carried on the possibility of using biotic factors for the activation of natural bonding forces present in lignocellulosic materials in order to reduce or eliminate the use of synthetic binders. Among the methods of activation, enzymatic treatment seems to be particularly promising. The concept of enzyme-catalysed bonding of lignocellulosic materials is based on the reactivity of functional groups of the aromatic compounds, such as lignin, which are engendered by oxidoreductases (laccase, peroxidase). Bonding of lignocellulosic materials can be performed either by means of a one-component system, which activates lignin contained in a raw material, or by a two-component system in which enzymatically activated technical lignins are mixed with the raw material, similar to conventional binding agent system. Annual plants, including fibrous ones (flax, hemp, jute, sisal, kenaf) due to a desirable combination of their physical and chemical properties, make a source of raw material for the manufacture of lignocellulosic composite materials for the purposes of the building and furniture-making industries and transport. The study was aimed at obtaining lignocellulosic composite boards by enzymatic bonding of annual plant waste material (shives, short fibres). The advantage of replacing synthetic binding agents with an enzymatic system of bonding lies in environmental protection and economic production.

### INTRODUCTION

The role played by laccase in higher plants has not been explained to the full extent as yet. Generally, it is assumed that laccase takes part in lignin degradation. On the other hand, the role of laccase in lignin biosynthesis remains unclear. The idea of bonding wood fibres *via* laccase-catalysed activation of the intercellular lamella was first conceived by Körner (1990) and the relevant process was described in a patent application by Kharazipour *et al.* (1993). The laccase enzyme can be used for bonding lignocellulosic materials by oxidation of phenol compounds, in accordance with the reaction equation given below:



In the course of an enzyme-initiated recombination of radicals, the lignin monomers undergo polymerisation to form a three-dimensional conjugated aromatic polymer. However, lignin, which is an easily available surplus product of the cellulose-processing industry, is currently commercially exploited up to 10% at the most. Therefore an idea appeared to convert, in an

appropriate way, this polyphenolic “waste” into interesting commercial products. Enzymatically-catalysed cross-linking of lignin by means of a “two-component glue”, occurring during the manufacture of wood-derived boards, can serve as an example.

## EXPERIMENTAL METHODS

### *Technical lignins*

Two kinds of black liquor of different concentration (Sample 1 and 2) were used for the manufacture of natural binding agents based on technical lignins. Chemical properties of the above black liquor samples, which were obtained during the dissolution of pine wood by the sulphate process, are presented in table 1.

*Table 1: Chemical properties of black liquors*

<i>Property</i>	<i>Black liquor</i>	
	<i>Sample 1</i>	<i>Sample 2</i>
<i>Organic matter content (%)</i>	94,1	81,3
<i>Lignin content (mg/g of organic matter)</i>	424	537

### *Enzymes*

To activate technical lignins, two different bacterial laccases from *Aspergillus sp.*, with Novo Nordisk, preparations were employed (Laccase 1 and 2). The black liquors were activated with enzymatic preparations in the activation conditions given in table 2.

*Table 2: Parameters of black liquor activation with Laccase 1 and 2*

<i>Parameter</i>	<i>Activation conditions</i>	
	<i>Laccase 1</i>	<i>Laccase 2</i>
<i>Temperature (°C)</i>	20	20
<i>pH</i>	4,5	4,5
<i>Time (h)</i>	1	1
<i>Dose</i>	3 LACU/g raw material dry substance (d.s.)	6 LAMU/g raw material dry substance (d.s.)

### *Board composites*

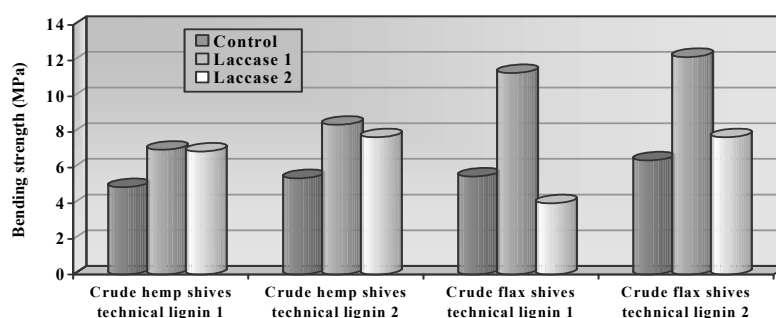
Board composites were made by bonding raw materials (crude hemp shives and crude flax shives) with the agents obtained and hot pressing them. The parameters of pressing were as follows: temperature - 140 °C, pressure - 2 MPa, time - 20 minutes.

## RESULTS AND DISCUSSION

Results of measurements carried out for the boards produced are presented in table 3 as well as in figure 1.

**Table 3: Physico-mechanical properties of boards manufactured by using binding agents based on technical lignins**

Kind of board	Technical lignin Sample 1		Technical lignin Sample 2	
	Density [kg/m <sup>3</sup> ]	Static bending strength [MPa]	Density [kg/m <sup>3</sup> ]	Static bending strength [MPa]
<i>Hemp</i>				
Control	723,5	4,9	712,1	5,4
Laccase 1	696,9	7,0	694,4	8,4
Laccase 2	685,1	6,9	655,8	7,7
<i>Flax</i>				
Control	751,6	5,5	732,5	6,4
Laccase 1	768,9	11,3	743,6	12,2
Laccase 2	725,2	4,0	734,6	7,7



**Figure 1: Bending strength of boards manufactured by using binding agents based on technical lignins**

In the case of hemp shives, an increase in bending strength was observed for samples 1 and 2 of technical lignins and for preparations Laccase 1 and 2. The increase in bending strength was particularly considerable in the case of boards produced from crude flax shives by using technical lignins activated with the preparation Laccase 1 both for sample 1 and 2. It can be seen from the results that properties of the boards were upgraded to a higher extent when technical lignins were activated with the preparation Laccase 1 rather than with the preparation Laccase 2 and when sample 2 of black liquor was used rather than sample 1.

## CONCLUSIONS

- Considerable increase in bending strength of the boards was achieved by the activation of technical lignins with the preparation Laccase 1, whereas the performance of the preparation Laccase 2 was lower, particularly in the case of crude flax shives.
- The application of binding agents based on sample 2 of black liquor to bonding of raw material resulted in boards of higher bending strength compared to binding agents based on sample 1 of black liquor. This fact originates from higher lignin content in organic matter of black liquor sample 2.
- A clear advantage of the process of manufacturing natural binding agents, in comparison with synthetic resins, is the absence of emission of harmful substances from the boards, both on the site of their production and on that of their prolonged use.
- The application of waste technical lignins as a natural glue opens the possibility of utilising lignins which make a surplus part of the biomass originated from renewable raw materials.

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Ghent University (RUG)  
Laboratory of Wood Technology  
Coupure links 653  
9000 GHENT  
BELGIUM



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