

Wood modification: Processes, Properties and Commercialisation

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Germany

The second European Conference on Wood Modification



Edited by
Holger Militz
and Callum Hill

WOOD MODIFICATION:
PROCESSES, PROPERTIES AND COMMERCIALISATION

THE SECOND EUROPEAN CONFERENCE ON WOOD MODIFICATION
ECWM 2005

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THE SECOND EUROPEAN CONFERENCE ON WOOD MODIFICATION ECWM 2005

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Wood modification: Processes, Properties and Commercialisation

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PREFACE

Wood is one of the most significant renewable resources utilised worldwide. Because of its mainly advantageous technological properties and its aesthetic value, wood is used in our modern living environment nearly everywhere. However, increasing quantities of fast growing softwood and hardwood species with inferior quality are being used worldwide, in order to protect virgin grown forests from deforestation.

To stay competitive with other, often non-sustainable materials (like plastics, metals *etc.*), researchers from universities, research institutes and industry are searching for novel treatment methods to upgrade the wood properties. Wood modification is one way of approaching these goals by chemically, physically or biotechnologically altering the wood cell wall.

Following the success of the First European Conference on Wood Modification (ECWM) held in Ghent, Belgium in April 2003, this Second ECWM in Göttingen again brings together researchers active in this relatively new research field from many parts of the world to share their knowledge and enthusiasm about the opportunities of wood modification.

The 1st ECWM as well this 2nd ECWM was organised by colleagues of the European funded “Thematic Network for Wood Modification”. This Network consists of partners from 15 European countries. Furthermore, because of the large interest in this item, this 2nd ECWM is jointly organised and supported by the European COST Actions E 37 “Sustainability through new technologies for enhanced wood durability” and E 44 “Wood processing strategy”.

The conference programme covers a broad range of related items. Technology already established in the market (like heat treatment processes) will be discussed, as well as new emerging technologies, fundamental results, and aspects of commercialisation.

Due to the time limitation of this two day conference, the organising committee had to select a maximum of 30 full papers from the large amount of abstracts sent in to the call for papers. To share the important knowledge of even more researchers, these proceedings consist furthermore of 33 poster presentation papers.

As chairman of the organising committee I would like to thank the sponsors of this event and wish all of you a very interesting and enjoyable conference.

Prof. Dr. Holger Militz

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CHAPTER 1

HEAT TREATMENT

THERMALLY MODIFIED WOOD (TMW) FOR PLAYGROUND TOYS: INVESTIGATIONS ON 13 INDUSTRIALLY MANUFACTURED PRODUCTS

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Keywords: Durability, mechanical properties, playgrounds, thermally modified wood

ABSTRACT

Within a research project at the Institute of Wood Technology Dresden (IHD), funded by the German Federal Ministry of Economic Affairs and Labour, 13 variants of thermally modified wood were investigated, focussing on their use for playground toys. Tests showed reduced strength properties, particularly impact strength, as known from other tests. Resistance against wood destroying fungi has clearly been improved, but the material differs considerably.

INTRODUCTION

Thermally modified wood (hereinafter referred to as "TMW") has been on the European market for 10 years. Because of its improved natural durability, it is predestined for exterior use. Although wood still is the most important material, there is strong competition with other materials like plastics or metals. This is caused particularly by:

- limited natural durability and service life,
- additional costs for maintenance,
- necessary impregnation by preservatives for use classes 3 and 4,
- partly limited effect of impregnation.

Some cases of failure of wooden toys/component parts (partly accompanied by accidents) have occurred over recent years in Germany (Scheiding *et al.* 2004). Also a lot of examples of decay damage was found in an IHD research project where about 100 elements of 40 playgrounds were investigated (Weiß 2002). The use of TMW might open new possibilities both to produce playground elements with a longer lifespan and to reduce the consumption of preservatives. Playground elements are not covered by building laws (*e.g.* European Construction Guideline), but have to guarantee security and stability as well under dynamic mechanical load.

The use of TMW hereby encounters a problem: Thermal treatment leads to decreased mechanical properties. Therefore, the aim of the project was examine the properties and performance of TMW material which is currently available on the European market and to investigate if and how the use of TMW for playground toys is possible.

EXPERIMENTAL

The investigations by IHD cover a wide range of available, industrially manufactured TMW products of 13 types of TMW from 9 European manufacturers, including 5 wood species (Table 1).

Table 1: Test material

nr.	manufacturer	wood variant	nr.	wood variant
1	a	TMW Scots Pine	20	reference Scots Pine sapwood
2	b	TMW European Ash	21	reference Scots Pine heartwood
3	b	TMW European Beech	22	reference Scots Pine impregnated*
4	c	TMW Scots Pine	23	reference European Beech
5	d	TMW Scots Pine	24	reference Norway Spruce
6	e	TMW Scots Pine	25	reference European Ash
7	f	TMW Norway Spruce		
8	g	TMW Norway Spruce		
			Common name	Scientific name
9	h	TMW Norway Spruce	Scots Pine	<i>Pinus silvestris</i> L.
10	i	TMW European Beech	Norway Spruce	<i>Picea abies</i> (L.) Karst.
11	i	TMW European Ash	European Beech	<i>Fagus sylvatica</i> L.
12	i	TMW Scots Pine	European Ash	<i>Fraxinus excelsior</i> L.
13	h	TMW Teak**	Teak	<i>Tectona grandis</i> L. f.

*) for hazard/use class 4 (weathered, ground contact)

***) round poles of largely sapwood

The target was to collect data from currently available material, produced on an industrial scale. The reference material (untreated wood) was from another origin. This has to be considered by comparison and in the assessment of the results.

In order to protect manufacturers' confidentiality, the material variants are given in a coded form. Data for thermally modified wood are indicated by "TMW ..."; reference materials are indicated only by the wood species name.

RESULTS AND DISCUSSION

Physical-mechanical investigations

The following properties were investigated:

- modulus of rupture (MOR)
- modulus of elasticity (MOE)
- impact bending strength
- Brinell hardness
- equilibrium moisture content under different climatic conditions
- differential swelling ratio

Results confirm changes in properties also known from other investigations (*e.g.* Welzbacher and Rapp 2002, Tjeerdma 2002, Illner *et al.* 2003). The specific data for density, modulus of rupture (MOR), modulus of elasticity (MOE) and impact strength are given in Table 2. In comparison to untreated wood, densities of TMW samples were reduced in Scots Pine and Norway Spruce by 20 % and at European Beech by 10 %. The strength properties, such as modulus of elasticity (MOE), were reduced in both hardwood and softwood by 20-30 %. The impact strength was reduced by 30-60 % on average. Noticeable differences between the Scots Pine variants were not found. TMW Norway Spruce No. 9 was found to be distinctly better than the other two TMW Norway Spruce variants.

Table 2: Density and strength properties

nr.	wood variant	density u1		MOR ¹		MOE ¹		Impact strength ¹	
		[kg/m ³]		[N/mm ²]		[N/mm ²]		[kJ/m ²]	
		x	s	x	s	x	s	x	s
1	TMW Scots Pine	419	26	62	18	10,302	810	25	12
4	TMW Scots Pine	401	25	69	9	8,023	1,177	22	6
5	TMW Scots Pine	422	64	71	27	9,122	2,794	16	8
6	TMW Scots Pine	390	24	69	12	7,680	1,237	20	3
20	Scots Pine sapwood	480	14	88	6	9,850	632	52	13
21	Scots Pine heartwood	552	44	98	8	11,478	1,219	47	5
	Scots Pine, literature ²	520		85		11,000		40	
7	TMW Norway Spruce	372	21	63	8	9,428	930	32	11
8	TMW Norway Spruce	388	48	61	14	8,643	1,903	19	6
9	TMW Norway Spruce	406	13	72	9	9,913	1,056	39	14
24	Norway Spruce	456	50	77	12	10,041	1,383	30	11
	Norway Spruce, lit. ²	460		80		11,000		46	
3	TMW European Beech	667	39	112	21	13,711	987	43	24
10	TMW European Beech	645	17	98	15	12,819	907	25	11
23	European Beech	739	12	124	6	11,784	720	176	39
	European Beech, lit. ²	710		120		14,000		100	
2	TMW European Ash	632	25	126	12	14,296	1,297	47	11
11	TMW European Ash	546	29	84	11	10,653	1,172	28	17
25	European Ash	593	35	72	10	5,790	896	34	13
	European Ash, lit. ²	700		105		13,000		68	
13	TMW Teak	427	44	64	14	9,393	1,913	29	15

¹) specimen conditioned in standard climate 20°C/65 %

²) medium values quoted from: Wagenführ/Scheiber: Holzatlas. Fachbuchverlag Leipzig 1989

Brinell hardness, an interesting value for flooring applications, was found to be reduced in comparison to untreated wood with TMW Scots Pine (av. 28 %), but not reduced with TMW Norway Spruce (Table 3). TMW hardwoods also showed distinctly reduced hardness values, referring to literature values: TMW European Beech -19 %, TMW European Ash -30 %.

Reactions to moisture

Moisture uptake of TMW, as an important benchmark for the treatment level, was reduced significantly. The EMC in four different standard climates 20/35, 20/65, 20/85 and 23/50 (each °C/RH) such as the differential swelling ratio were determined. EMC was reduced by 50 % on average (Table 4).

The differential swelling ratio (size change percentage per moisture percentage) was found to be reduced in TMW softwoods by 30 %, compared to untreated wood or the literature value. The average differential swelling ratio for TMW softwood was calculated by 0.17%/%, in comparison with the average value for of softwood according to DIN 1052 by 0.24 %/ %.

TMW hardwood variants, European Ash and European Beech, showed no noticeable differences.

Table 3: Density and Brinell hardness

Nr.	wood variant	density u ¹		hardness ¹ radial		hardness ¹ tangential	
		x	s	x	V	x	V
		[kg/m ³]	[kg/m ³]	[N/mm ²]	[%]	[N/mm ²]	[%]
1	TMW Scots Pine	419	26	11	11	12	26
4	TMW Scots Pine	401	25	14	19	11	15
5	TMW Scots Pine	422	64	15	35	16	33
6	TMW Scots Pine	390	24	15	28	11	15
20	Scots Pine sapwood	480	14	16	23	15	13
21	Scots Pine heartwood	552	44	19	20	20	10
	Scots Pine, literature ²	520		19		19	
7	TMW Norway Spruce	372	21	12	17	11	27
8	TMW Norway Spruce	388	48	12	19	13	10
9	TMW Norway Spruce	406	13	12	12	12	12
24	Norway Spruce	456	50	13	16	14	9
	Norway Spruce, literature ²	460		12		12	
3	TMW European Beech	667	39	31	22	26	7
10	TMW European Beech	645	17	28	14	26	17
23	European Beech	739	12	31	3	27	6
	European Beech, literature ²	710		34		34	
2	TMW European Ash	632	25	32	24	28	9
11	TMW European Ash	546	29	24	18	23	9
25	European Ash	593	35	20	13	26	16
	European Ash, literature ²	700		41		41	
12	TMW Teak	427	44	10	4	10.8	4

¹) specimen conditioned in standard climate 20°C/65 %

Table 4: Equilibrium moisture content (EMC) in different climates; differential swelling ratio

nr.	wood variant	EMC [%]				differential swelling ratio [%/%]			
		20/35	20/65	20/85	23/50	radial		tangential	
		x	s	x	s	x	s	x	s
1	TMW Scots Pine	4.7	6.5	9.3	6.3	0.13	0.05	0.31	0.06
4	TMW Scots Pine	6.0	6.6	11.4	7.0	0.15	0.09	0.32	0.06
5	TMW Scots Pine	4.8	5.5	8.4	6.1	0.10	0.04	0.27	0.11
6	TMW Scots Pine	5.1	5.6	9.2	6.1	0.11	0.03	0.29	0.07
12	TMW Scots Pine	4.9	5.7	9.5	6.4	0.14	0.02	0.33	0.03
20	Scots Pine sapwood	9.0	13.2	18.3	-	0.17	0.02	0.34	0.02
21	Scots Pine heartwood	9.1	12.3	16.9	10.7	0.21	0.02	0.37	0.03
	Scots Pine, literature ²					0.19		0.36	
7	TMW Norway Spruce	4.1	5.1	9.6	5.4	0.12	0.03	0.28	0.03
8	TMW Norway Spruce	4.2	5.0	8.7	5.4	0.11	0.03	0.24	0.03
9	TMW Norway Spruce	5.1	5.6	9.2	5.1	0.16	0.03	0.30	0.02
24	Norway Spruce	8.6	12.3	18.6	11.5	0.20	0.03	0.35	0.02
	Norway Spruce, literature ²					0.19		0.36	
3	TMW European Beech	3.7	4.9	6.3	4.7	0.21	0.04	0.45	0.07
10	TMW European Beech	4.3	5.0	8.2	4.8	0.22	0.03	0.40	0.03
23	European Beech	8.3	11.5	18.5	11.0	0.21	0.02	0.42	0.02
	European Beech, literature ²					0.20		0.41	
2	TMW European Ash	5.3	7.6	10.9	6.4	0.19	0.03	0.35	0.06
11	TMW European Ash	3.5	4.4	6.4	4.6	0.19	0.05	0.27	0.04
25	European Ash	7.8	10.8	14.9	10.0	0.16	0.01	0.30	0.01

²) literature value quoted from: Holz-Lexikon. DRW-Verlag Leinfelden-Echterdingen 2003

For additional practical information, the accuracy of moisture measurement by the electrical resistance method, in comparison to the oven-dry method, was examined. The TMW samples had been conditioned at standard climate 20/65. The deviation of the instrument (Hydromette RTU 600) values varied between -0.5 % up to +2.4 %, on average +1 %. Therefore the electrical method seems to be applicable also for TMW.

Biological investigations

The biological investigations were focussed on:

- natural durability – laboratory tests (EN 113, EN 152, EN ISO/IEC 60068-2-10)
- natural durability – field tests (EN 252, double-layer test)
- natural durability – field tests (weathering by exposure 0° and 45°)
- assessment of mould rot and blue stain growth (lab and field tests)

Resistance against wood destroying fungi

For classification acc. to EN 113 (basidiomycetes), those fungus species have to be used which lead to the highest mass loss in specimen and thus to the worst durability class, respectively.

The classification of resistance against soft rot is based on that period when the controls (European Beech, Scots Pine sapwood) showed a mass loss of 20 %, which is 16 weeks for European Beech and 32 weeks for Scots Pine.

Results are given in Table 5; the durability values for final analysis are typed in bold numbers. Significant improvements of the natural resistance against wood destroying fungi were observed, as expected and known from other investigations. The obtained durability classes deviated from 4 "slightly durable" to 1 "durable". It is obvious that *Poria placenta* attacks softwood TMW more than other test species, as tests by Welzbacher and Rapp (2002) and Hanger *et al.* (2002a) have shown likewise.

The unexpected results for TMW European Beech in particular correspond with other previous results (*e.g.* Hanger *et al.* 2002): from durability class 5 "not durable" TMW Beech was improved by thermal treatment to classes 1 "very durable" and 2 "durable".

Resistance against mould

Mould is rather a visual problem. Firstly it was assumed that thermal treatment is also effective against mould. Although mould growth was observed (see Table 6), the mycelium does not grow as deeply into the TMW as in untreated wood, as microscopic investigations showed. This may be caused by the lower nutrient content (hemicellulose) and the lower EMC of TMW.

Resistance against blue stain

As result of the tests according to EN 152, all TMW and control specimens were fully or partly coloured by blue stain on the surfaces. A quantitative assessment of this growth was not possible. The cross-section of the non-treated specimen (Norway Spruce, Scots Pine sapwood) after cross-cutting showed full colouration by blue stain. All

TMW variants and the untreated hardwood were not coloured by blue stain. A general resistance of TMW against mould and blue stain is not to be expected, and was not ascertained. Therefore only improved resistance of TMW against wood destroying fungi should be discussed.

Table 5: Resistance classes acc. to EN 350-1 (control species: Scots Pine sapwood for softwoods, European Beech for hardwoods)

nr.	wood specie	resistance class acc. to EN 350-1 and EN 113 (without leaching)			durability class acc. to ENV 807 (soft rot)
		Coniophora puteana	Gloeophyllum trabeum	Poria placenta	
1	TMW Scots Pine	1	1	3	3
4	TMW Scots Pine	2	2	4	3
5	TMW Scots Pine	1	1	2	3
6	TMW Scots Pine	2	1	3	3
12	TMW Scots Pine	1	2	4	3
7	TMW Norway Spruce	1	2	2	1
8	TMW Norway Spruce	1	2	4	3
9	TMW Norway Spruce	2	1	4	3
24	Norway Spruce	5	5	5	4
		Coniophora puteana	Gloeophyllum trabeum	Trametes versicolor	
3	TMW European Beech	1	1	1	1
10	TMW European Beech	1	1	2	1
2	TMW European Ash	2	2	1	3
11	TMW European Ash	1	1	1	1
25	European Ash	3	2	4	4

Table 6: Assessment of mould resistance

nr.	wood variant	assessment level	assessment key
20	Scots Pine sapwood untreated	2	
21	Scots Pine heartwood untreated	1	0
24	Norway Spruce untreated	2	mould growth non visible (without help by instruments)
1	TMW Scots Pine	1	
4	TMW Scots Pine	1	1
5	TMW Scots Pine	1	mould growth visible, distinctly weaker than in European Beech control specimen
6	TMW Scots Pine	1	
7	TMW Norway Spruce	1	
8	TMW Norway Spruce	1	
9	TMW Norway Spruce	1	2
25	European Ash untreated	2	mould growth visible, distinctly stronger than in European Beech control specimen
3	TMW European Beech	2	
2	TMW European Ash	2	

Field tests

Complementing the lab tests, durability field tests according to EN 252 and the double layer test (designed by Rapp) were started in autumn 2003. Previous mid-term evaluations had been carried out 12 months after the test start, with the following results:



Figure 1: Playground toy with TMW by ABC team

The EN 252 samples showed slight discolouration. The moisture content of the upper parts (above ground) of the TMW specimen was between 4-10 % (untreated specimen 13-16 %); the lower parts (in the ground) showed 43-78 % (untreated wood 37-81 %). This emphasises that - although the moisture uptake of TMW cell walls is reduced - the lumina (cell cavities) may take up fluid water, similar to untreated wood. The double layer test showed discolouration on the upper side of TMW specimen already after three months, but even after one year no discolouration occurred on the inner and lower surfaces. All control specimens were strongly discoloured. For both the EN 252 and double layer tests, no attack by wood destroying fungi occurred in the TMW specimen (destruction ratio "0"). The results of laboratory tests on natural durability are not sufficient to describe the durability under practical conditions (as recently confirmed by Rapp *et al.* 2005). Weathering leads to greying of TMW; partial mould attack occurred on the surface. Some TMW specimens from the EN 252 test in ground contact showed attack by insects.

CONCLUSIONS

TMW is appropriate in principle as a construction material for playground toys. The strength properties are reduced considerably, as known from other investigations. To evaluate test results accurately, the source of reference values (*e.g.* from untreated wood, literature) has to be taken into account; particularly the fungal species of biological tests have to be considered for assessment of durability test results.

The impact bending strength (increased brittleness) might be the limiting factor particularly because of dynamic-mechanical loads (*e.g.* swing beam). Load tests of component parts (original dimensions) have to be carried out. A mix of materials including TMW might be a good compromise; actual TMW is available as round timber up to 180 mm, beams up to 95 × 95 mm² and glulam up to 145 × 145 mm².

Many customers expect a usability of TMW for hazard/use class 4 (soil contact), which requests a natural durability class 1 (very durable; acc. to EN 460). However, manufacturers mostly declare usability only for use class 3 (without ground contact). The very high durability classes found by laboratory tests for some materials (even European Beech) might offer use in soil contact; long-time field tests have to confirm this assumption.

Although the use of thermally modified wood for playground toys, also in load-bearing uses, is possible in principle, the specific application case has to be checked properly. There is a high interest of playground toy manufacturers for TMW; first playgrounds with TMW elements and component parts have been introduced meanwhile, *e.g.* by the German companies ABC team (Fig. 1) or Sport Gerlach.

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BIOLOGICAL AND MECHANICAL PROPERTIES OF DENSIFIED AND THERMALLY MODIFIED NORWAY SPRUCE

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Keywords: Densification, durability, mechanical strength, oil-heat treatment, thermal modification

ABSTRACT

For the first time, untreated Norway spruce (*Picea abies* Karst.) was densified in a common industrial scale process and afterwards thermally modified in an Oil-Heat treatment process. Biological and mechanical properties were investigated on axially matched samples. Wetting and drying cycles were performed to determine the change in dimensional stability of densified and heat treated samples compared to references. Biological tests of resistance to basidiomycetes on malt agar according to EN 113 (1996) and soil block tests according to prEN 807 (2001) showed substantially reduced mass losses with densified heat treated material, compared to untreated controls. According to the classification of natural durability (EN 350-1, 1994) the densified and Oil-Heat treated material was classified as 'very durable' (durability class 1). The bending strength of densified and Oil-Heat treated material was only slightly reduced compared to untreated Norway spruce. The MOE of densified and Oil-Heat treated material was increased by 42 %, whereas the impact bending strength was decreased by 44 % compared to untreated Norway spruce controls. Densified and thermally modified samples showed improved dimensional stability compared to untreated densified material.

INTRODUCTION

The natural durability of most European wood species restricts the use of wood without wood preservation in outdoor applications. As an alternative to chemical preservation systems, thermal modification processes as non-biocidal techniques of wood protection were developed and promoted in recent years (Leithoff and Peek 1998). Thermal treatments improve some wood properties, e.g. dimensional stabilisation and decay resistance (Militz and Tjeerdsma 2001, Rapp and Sailer 2001), but also reduce the strength properties of wood (Bengtsson *et al.* 2002, Brischke and Rapp 2004). To overcome this disadvantage of decreased strength, thermo-mechanically densified material with increased initial strength properties compared to non-densified wood was applied to an Oil-Heat treatment process.

Densification of solid wood is an established process to improve selected mechanical and physical properties e.g. MOE, MOR, surface hardness, transversal shear strength and dimensional stability (Morsing 1997, Navi and Girardet 2000). The combination of mechanical load in the radial direction and elevated temperatures during the densification process has been studied since the beginning of the 20th century (Kollmann 1936, Seborg *et al.* 1945). Nevertheless, the transformed

compression-set during densification is unstable and leads to set-recovery under the influence of liquid water or even elevated moisture.

Prior examinations on densified wood predominately deal with the problem of dimensional stabilisation, fixation of set-recovery and increased mechanical properties. In contrast, this study was concerned with the examination of the biological properties of densified wood, in particular the change in natural durability due to a densification process with elevated temperatures and an subsequent Oil-Heat treatment to stabilise the compression set.

EXPERIMENTAL

Material

Untreated Norway spruce (*Picea abies* Karst.) with an average density of 0.52 g/cm³ at an initial moisture content of 12 % was applied to the thermo-mechanical densification process. Untreated non-densified and untreated densified spruce was furthermore thermally modified by an Oil-Heat Treatment (OHT) process. Besides the densified and thermally modified material, untreated pine sapwood controls (*Pinus sylvestris* L.), untreated Norway spruce, Douglas fir heartwood (*Pseudotsuga menziesii* Franco), oak heartwood (*Quercus petraea* Liebl.) and pine sapwood specimens vacuum-impregnated in a treating solution containing 0.7 % and 2.8 % CCB were used in the biological tests as references. All samples were cut into the respective test specimens and tested at the Federal Research Centre for Forestry and Forest Products (BFH), Hamburg, Germany.

Thermo-mechanical densification and Oil-Heat treatment

Solid spruce samples of 1000 x 150 x 40 mm³ were densified in radial direction by 'Deutsche Holzveredelung Alfons & Ewald Schmeing oHG', Kirchhundem, Germany, using a conventional industrial hot press. The intermittent thermo-mechanical densification process was divided into three steps: heating up, compression, and cooling/conditioning, wherein the heat transmission was achieved by contact of the samples with the heated upper and lower press plates. A diagram of the densification process is given in Figure 1.

Untreated non-densified and densified spruce specimens of 500 x 140 x 20 mm³ were thermally modified by an Oil-Heat treatment at 220°C for four hours at BFH. The treatment temperature was measured inside the specimens by means of thermocouples.

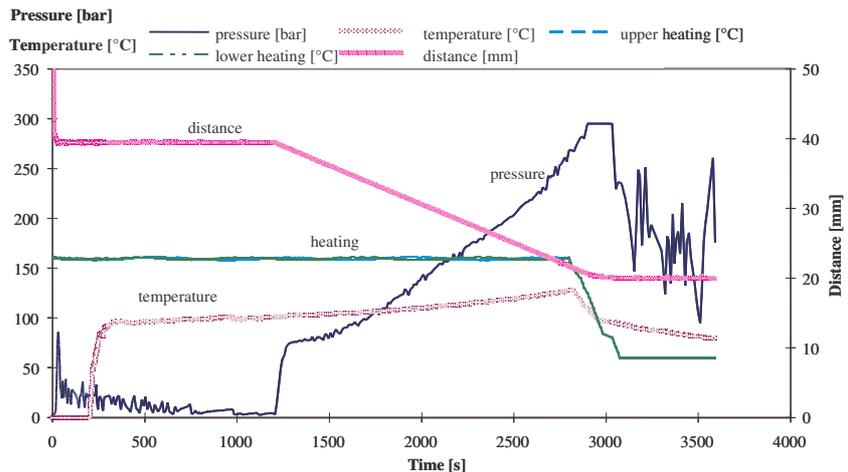


Figure 1: Scheme of a distance controlled densification process for compression of solid wood from 40 mm to 20 mm

Resistance to basidiomycetes

The resistance to basidiomycetes was tested according to EN 113 (1996) with the following alterations: $n = 10$ specimens of $40 \times 10 \times 10 \text{ mm}^3$ were incubated in large Petri dishes (120 mm diameter) for 12 weeks. In preliminary tests with brown and white rot causing fungi (Welzbacher and Rapp 2002), *Poria placenta* caused the highest mass losses on heat treated wood compared to all other tested fungi, including *Coniophora puteana* and *Coriolus versicolor*. Therefore, the following strain was used for the study: *Oligoporus placenta* var. *Monticula* = (Fr.) Gilbertson et Ryv. FPRL 280 BAM, 8/1997.

To assess the grade of durability, the relative durability was calculated as the quotient of mass loss of the tested material and untreated Scots pine sapwood controls (X-Value, EN 350-1 1994), as is normally done for the classification of naturally durable timber.

Resistance to soft-rotting micro-fungi and other soil inhabiting micro organisms

The resistance to soft-rotting micro-fungi was tested according to prEN 807 (2001). Therefore $n = 20$ specimens of $100 \times 10 \times 5 \text{ mm}^3$ were incubated for 32 weeks in natural top soil substrate (compost and test fields) from two different areas at BFH in Hamburg, Germany.

Mechanical testing

The bending strength (MOR) and the MOE was determined in a three point bending test according to DIN 52 186 (1978) with $n = 40$ specimens of $200 \times 10 \times 10 \text{ mm}^3$.

Impact bending strength was tested according to DIN 52 189 (1981) applied on $n = 40$ specimens of $200 \times 10 \times 10 \text{ mm}^3$ using a Louis Schopper pendulum impact machine.

Dimensional stability

Specimens of $10 \times 20 \times 20 \text{ mm}^3$ ($n = 20$) were cut from non-densified Norway spruce and densified Norway spruce, both heat-treated and untreated. Eight cycles of oven drying at 103°C for 24 h followed by a

soaking phase by means of water pressure impregnation at 8 bar/20 min with subsequent water storage of 24 h at 60°C were performed to determine the change of dimensional stability due to densification and heat treatment. Swelling and shrinking was measured after each wetting and drying phase in radial direction by determining the radial length.

RESULTS AND DISCUSSION

Resistance to basidiomycetes

Both processes, the thermo-mechanical densification and the Oil-Heat treatment, applied to spruce specimens, resulted in significantly increased resistance against fungal decay, compared to the mass loss found in untreated spruce (Figure 2). Untreated spruce showed a mass loss of 30.7 %, a significantly lower mass loss of 7.5 % was observed in densified spruce wood. An average weight loss of 8.9 % was found for Oil-Heat treated spruce (spruce OHT), whereas densified and Oil-Heat treated spruce (densified spruce OHT) exhibited a mass loss of 0.8 % only.

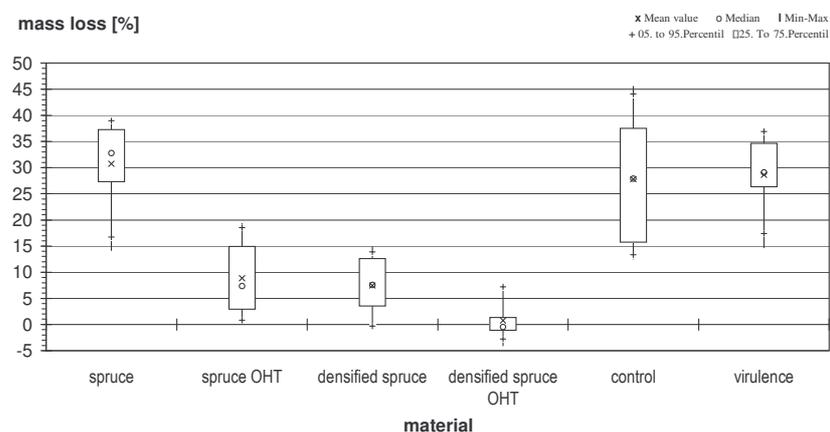


Figure 2: Mass loss after fungal attack by *Poria placenta*

The effect of increased resistance against fungal decay of densified wood compared to controls was also observed by Welzbacher *et al.* (2004) and Schwarze and Spycher (2005). In both studies, Norway spruce specimens, subjected to the two-stage THM procedure of Navi and Girardet (2000), were tested. In tests with *Poria placenta* Schwarze and Spycher (2005) found an average mass loss of about 13 % in densified spruce (21 % in controls), whereas Welzbacher *et al.* (2004) observed 27 % mass loss in densified specimens (36 % in controls). Nevertheless, a post-treatment of the densified specimens at 180°C for 30 min in saturated steam conditions only reduced the mass loss slightly to 10 % (Schwarze and Spycher 2005), and 17 % respectively (Welzbacher *et al.* 2004). The influence of a steam post-treatment on durability seems to be negligible compared to the impact of an Oil-Heat treatment.

Resistance to soft-rotting micro-fungi

A compost substrate was used to determine the resistance against soft-rotting micro-organisms, since it generated higher mass losses in the specimens compared with the field substrate. The mass loss of

densified and non-densified spruce specimens was reduced significantly by an Oil-Heat treatment (Figure 3).

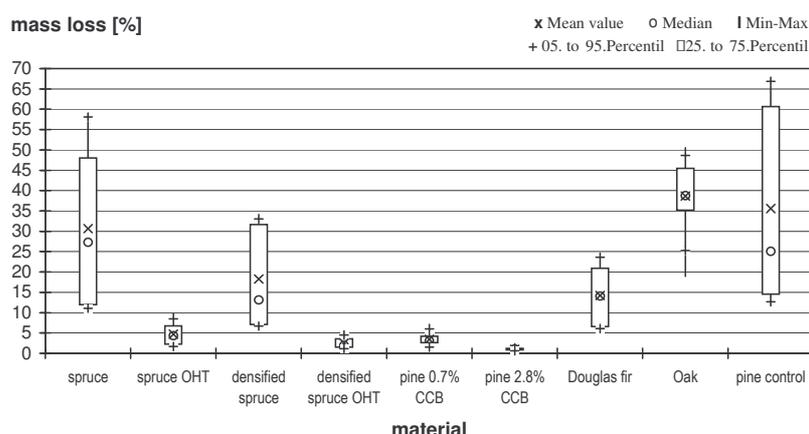


Figure 3: Mass loss after 32 weeks exposure in compost soil according to prEN 807 (2001)

A mass loss of 30 % was found in untreated spruce and about 18 % in densified spruce specimens. Oil-Heat treated specimens showed significantly lower values: 5 % mass loss was observed in spruce OHT, whereas 3 % mass loss occurred in densified spruce OHT. The Oil-Heat treatment increased the resistance against decay to a higher extent than the densification. The highest increase in durability was found as a result of both processes combined. This can be seen from the classes of natural durability according to EN 350-1 (1994) based on the tests according to prEN 807 (2001) and based on the tests according to EN 113 (1996), as listed in Table 1.

Table 1: Density of the different materials tested and assigned classes of natural durability according to EN 350-1 (1994) based on absolute (g-basis) and proportional (%-basis) mass loss after biological tests according to EN 113 (1996) and prEN 807 (2001)

material	oven dry	durability classification based on		durability classification based on	
	density	tests according to EN 113		tests according to prEN 807	
	[g/cm ³]	on g-basis	on %-basis	on g-basis	on %-basis
spruce	0.48	5	5	4	5
spruce OHT	0.43	2	3	1	1
densified spruce	1.08	3	3	4	3
densified spruce OHT	0.86	1	1	1	1

Spruce was classified as not durable (class 5) in tests with *Poria placenta* as well as in tests in compost soil against soft-rotting micro-organisms. As a result of the thermo-mechanical densification, durability class 3 (moderately durable) was achieved by densified spruce. An Oil-Heat treatment increased the natural durability to a greater extent: spruce OHT was durable to moderately durable (class 2-3) in tests according to EN 113 (1996), and very durable (class 1) in tests according to prEN 807 (2001) respectively. In addition, the combination of densification and subsequent Oil-Heat treatment resulted in durability class 1 (very durable) in both applied biological tests.

Mechanical testing

Densification of solid Norway spruce improved MOR, MOE and Impact bending strength significantly (Table). This is causally connected to increased density (Morsing 1997, Navi and Girardet 2000, Heger *et al.* 2004).

Table 2: Average values of density, MOR, MOE and impact bending strength; untreated spruce is taken as basis for proportional examination of mechanical properties

material	density	MOR		MOE		Impact bending strength	
	[g/cm ³]	[N/mm ²]	[%]	[N/mm ²]	[%]	[kJ/m ²]	[%]
spruce	0,50	108,0	100	13966	100	31,8	100
spruce OHT	0,43	84,7	78	12304	88	16,5	52
densified spruce	1,09	209,3	194	23577	167	38,2	120
densified spruce OHT	0,86	105,0	97	19815	142	17,7	56

The Oil-Heat treatment reduced the MOR of densified spruce significantly by 50 %, but densified spruce OHT still had an average MOR equal to untreated spruce. The influence of the Oil-Heat treatment on the dynamic strength was more critical: Impact bending strength of densified spruce OHT was reduced by 44 % compared to spruce (Table 2). The influence of the heat treatment on MOE was rather negligible, since MOE of densified spruce OHT was still increased about 50 % compared to untreated spruce.

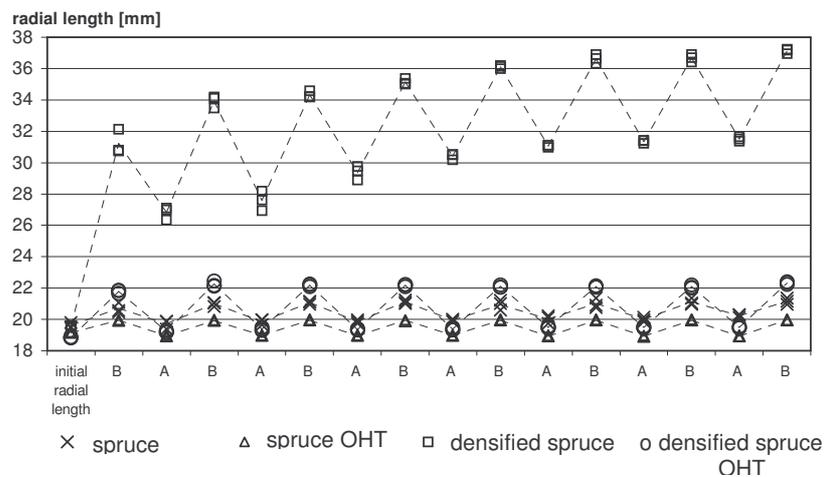


Figure 4: Radial swelling and shrinking after eight cycles of oven drying at 103 °C for 24 h (A) followed by water pressure-impregnation at 8 bar/20 min and subsequent water storage for 24 h (B)

Dimensional stability

After eight cycles of wetting and drying, densified spruce specimens showed maximum swelling in radial direction of about 88 %, whereby a set-recovery of approximately 60 % was observed (Figure 4). Thermal modification resulted in a significantly decreased maximum swelling (19 %) and in addition, permanent fixation of compression-set was achieved (set-recovery 3.5 %). This is exactly what Heger *et al.* (2004) observed on THM-densified wood, since the set-recovery was below 3 % and maximum swelling in a range from 15 to 20 % after post-treating the THM-densified specimens at 180 °C for 30 min.

CONCLUSIONS

Both, the post-treatment according to Heger *et al.* (2004) as well as the Oil-Heat treatment achieved permanent fixation of compression-set of densified spruce. In contrast to the steam-post-treatment, significantly increased durability was a result of an Oil-Heat treatment. As a drawback, the dynamic mechanical properties of densified and Oil-Heat treated spruce were reduced by 40 % compared to controls, though static bending strength was equal to untreated spruce.

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THERMO-GRAVIMETRIC ANALYSIS AS A TOOL FOR THE OPTIMISATION OF WOOD HEAT TREATMENT PARAMETERS

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Keywords: Heat treatment, thermo-gravimetric analysis, wood pyrolysis, time temperature equivalence

ABSTRACT

Retification is a heat treatment that decreases the swelling of wood and increases its resistance to fungal attack. It consists of a mild pyrolysis of wood (180°C-260°C) that takes place in a non oxidative atmosphere (nitrogen). The industrial development of retification requires the optimisation of the treatment temperature and duration. In order to enhance the homogeneity of temperature in the oven, and to avoid exothermic reaction, low temperatures seem to be preferable to high temperatures. Although duration and temperature of treatment have to be high enough to provide good biological resistance and stabilisation to the wood, high temperatures lead to a loss of mechanical strength. A question arises from these previous observations: is there any equivalence between a treatment of short time carried out at high temperature and a treatment of longer time at lower temperature? Answering this question can help to optimise retification temperature and duration. The purpose of this study is to evaluate the relevance of a "time temperature equivalence" (TTE) for wood pyrolysis in the temperature range of retification. The principle of TTE is adapted from the study of wood viscoelastic properties. In this study, it is applied to the rate of anhydrous weight loss during wood pyrolysis. Thermo-gravimetric analysis (TGA) was performed on maritime pine (*Pinus pinaster* Ait.) and beech (*Fagus sylvatica*) wood powder. Isothermal degradations were carried out at different temperatures, ranging from 160°C to 260°C. A specific data analysis was carried out on the TGA derivative (DTG) in order to assess the relevance of the TTE in the temperature range of retification. It gave interpretable results for maritime pine, but not for beech. It showed that for maritime pine wood the TTE is confirmed from 200°C to 220°C, and not confirmed for temperatures higher than 230°C. An optimisation of the temperature and time of treatment is thus possible.

INTRODUCTION AND THEORETICAL CONSIDERATIONS

Short presentation of retification treatment

Retification (Armines 1986) is a heat treatment which consists of a mild pyrolysis of wood (180°C-260°C). It takes place in a non oxidative atmosphere (nitrogen). This treatment decreases the swelling of wood (Repellin and Guyonnet 2005) and increases its resistance to fungal attack (Kamdem *et al.* 2002, Mouras *et al.* 2002) without the use of chemicals. However, the main drawback of wood heat treatment is an significant decrease of mechanical strength (Repellin and Guyonnet 2003).

As a consequence, the commercial and industrial development of retified wood would be made easier, if it were possible to minimise the loss of mechanical strength. The purpose of this study is to investigate the possibility to optimise heat treatment parameters (duration and temperature) in order to minimise the loss of mechanical strength.

Wood pyrolysis

Wood pyrolysis follows two pathways: slow and fast pyrolysis, which involves many different reactions and products (Shafizadeh 1984, Faix *et al.* 1991). For temperatures ranging between 200 and 280°C, both slow and fast pyrolysis are present, but slow pyrolysis predominates. The main products of wood decomposition by slow pyrolysis are water, carbon dioxide, carbon monoxide, formic acid, acetic acid and furfural.

At temperatures in excess of 300°C, fast pyrolysis is predominant. Wood constituents decompose rapidly to form tar and volatiles of low molecular weight such as methane, formaldehyde, methanol, phenol, *etc.* These decompositions are exothermic reactions.

Table 1: Relationship between low temperature pyrolysis gaseous products and chemical modifications

Product of degradation	Chemical reaction ^a	Chemical reaction ^b
water	Hemicelluloses degradation	Drying and dehydration
carbon dioxide	Decarboxylation of uronic acids of hemicelluloses and pectins	Hemicellulose and lignin decarboxylation
methanol	Decomposition of 4-O-methyl groups of uronic acids Decomposition of lignin's syringyl and guaiacyl units	Degradation of hydroxymethyl groups of lignin and hemicelluloses
acetic acid	hydrolysis of O-acetyl groups of xylan chains.	Degradation of acetyl groups of hemicelluloses
formic acid	No explanation	No explanation
furfural	No explanation	Pentosans degradation

^a According to DeGroot *et al.*

^b According to Weiland *et al.*

Retification occurs between 180°C and 260°C. Consequently, the gaseous products evolved during retification are mainly those of slow pyrolysis. Degroot *et al.* (1988) studied the isothermal decomposition of poplar sapwood (*Populus trichocarpa*) at 250°C. Weiland *et al.* (1998) studied the chemical modification of wood powder of chestnut (*Castanea sativa*), Norway pine (*Pinus sylvestris*) and maritime pine (*Pinus pinaster* Ait.-) from room temperature to 350°C. The relationship between the evolved gases and the corresponding degradation mechanisms are presented in Table 1, as proposed by these two authors.

It can be seen (Table 1) that the evolved gases come mainly from hemicelluloses and lignin degradation. Nevertheless, cellulose degradation is not excluded. It is known that gases released during cellulose degradation by pyrolysis are water, carbon monoxide, and carbon dioxide (Browne 1958), and these three gases (Weiland *et al.* 1998) are indeed released during retification. Thus, the degradation of

all three constituents of wood (hemicelluloses, lignin and cellulose) may occur during heat treatment of wood.

Cellulose is often considered as responsible for the mechanical strength of wood. Consequently, as soon as cellulose begins to decompose, loss of mechanical strength may take place. Nevertheless, hemicelluloses may also play an important part in wood strength. Some authors found a correlation between the decrease of mechanical strength and the degradation of hemicelluloses by brown-rot fungi (Winandy 1993).

Hypothesis concerning pyrolysis reactions

It is postulated here that the reactions involved in wood pyrolysis may be classified into two groups. Both groups induce an increase of stabilisation and durability and a decrease of mechanical strength. However, the first group favours stabilisation and durability whereas the second favours mechanical strength loss (Table 2). In the range of retification treatment temperatures, a competition between these two groups is likely to happen.

Table 2: The postulated two groups of wood pyrolysis reactions.

Properties modification	First group	Second group
Increase of stability	++	+
Increase of durability	++	+
Decrease of mechanical strength	+	++

At low temperatures (200°C) only slow pyrolysis reactions (first group) may be taken into account. Other reactions can be neglected.

When the treatment temperature increases, fast pyrolysis reactions and cellulose destruction (second group) are enhanced.

According to these hypotheses, it would be profitable to carry out the heat treatment at low temperatures. At the same time, the improvement of wood end use properties depends on the extent of the treatment. The material modification (that matches to the anhydrous weight loss) must be sufficient to provide good biological resistance and stabilisation to the wood. Thus, a decrease in temperature of treatment should be associated with an increase in the treatment duration, since anhydrous weight loss increases both with increasing temperature and duration.

Both reactions of the first and second group obviously result in anhydrous weight loss. Put another way, anhydrous weight loss is the only means to control the advancement and the rate of wood pyrolysis. The rate of anhydrous weight loss should depend on the type of reaction involved. In particular, reactions of the first group and reactions of the second group should result in different values of the rate of anhydrous weight loss.

On this basis, if the contribution of each group of reactions is the same over the range of temperature (180°C to 260°C), then, there should be an equivalence between a short treatment time carried out at high temperatures and a treatment of longer time at lower temperatures, as regards the rate of anhydrous weight loss.

The purpose of this study is thus to evaluate the relevance of a “time temperature equivalence” (TTE) for wood pyrolysis in the temperature range of retification.

Principle of time temperature equivalence (TTE)

The principle of TTE is adapted from the study of wood viscoelastic properties (Pluvinage 1992). It may be expressed as follows. The value of a measurable quantity is the same at a high temperature for a short time as at a low temperature for a long time.

The TTE principle is observable for instance, when measuring the dynamic flexural vibration of wood beams. For a given range of frequencies, the real part of the complex modulus of elasticity has the same value whether it is measured at a high temperature for a short time of exposure, or at a low temperature for a long time of exposure.

Consider a quantity R, that can be measured on a wood sample at two different temperatures (T_{ref} and T) that belong to a given range of temperatures. The TTE is verified if: for any value of R, the time t (that taken to reach R at temperature T) and the time t_{Tref} (that taken to reach R at temperature T_{ref}) are linked (Eqn. 1):

$$t_T = \frac{t_{Tref}}{\alpha_T} \tag{1}$$

Where α_T is called the translation factor. It depends only on the temperature and it is constant versus time. The TTE principle can also be written (Eqn. 2):

$$R=R(t_{Tref},T_{ref})=R(t_T,T)=R(t_{Tref}/\alpha_T,T) \tag{2}$$

And Equation 1 leads to:

$$\ln(t_T)=\ln(t_{Tref})-\ln(\alpha_T) \tag{3}$$

According to Equations 2 and 3, when R is plotted against $\ln(t)$, isothermal curves can be superposed by a translation of $\ln(\alpha_T)$ (Figure 1).

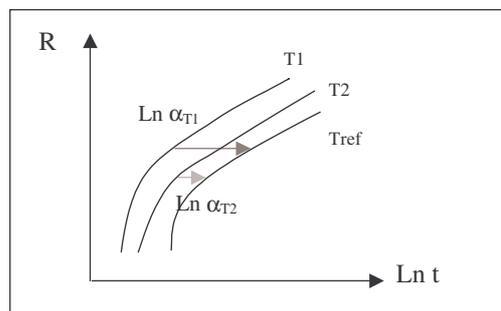


Figure 1: Principle of time temperature equivalence

Thus, an equivalence between the effect of treatment duration and the effect of treatment temperature can be found when any isothermal curve superposes on the isothermal curve obtained at T_{ref} , by horizontal translation (Figure 1).

In order to check if the TTE principle is confirmed in the temperature range of retification, thermo-gravimetric analysis (TGA) was carried out. Isothermal DTG (TGA derivative) curves were plotted and analysed, in order to assess the relevance of the TTE in the temperature range of retification, with regard to the rate of anhydrous weight loss. In this study, R is a given value of the DTG.

The purpose of this study

This study aims to test the TTE with regard to the rate of anhydrous weight loss, in the range of temperature of retification (180-260°C). If this TTE principle is confirmed over a given range of temperatures, the modification of the material will be the same at any temperature in this particular range for a given anhydrous weight loss. In this temperature range, it will be possible to increase the temperature and reduce the duration without further degradation of wood constituents due to the second group of reactions. However, if the temperature exceeds the temperature range where the TTE is verified, the second group of reactions will induce further degradation of some of the material constituents and increase the loss of strength of the material.

EXPERIMENTAL

Samples

Natural wood powder was obtained by grinding and sieving specimens between 150 and 212 μm . The samples were made of 10 mg of wood powder. Two species were studied: maritime pine (*Pinus pinaster* Ait.) and beech (*Fagus sylvatica*). Before experiment, these samples were stored at room temperature in ambient conditions.

Method

The device was a thermobalance NETSCH TG 209. The temperature program was set as follows:

- a ramp from 30°C to 150°C at 30°C/min
- an isotherm at 150°C for 20 min, in order to dry the sample until its anhydrous state
- a ramp from 150°C to the chosen temperature (from 160°C to 260°C), at 99°C/min
- an isotherm at the chosen temperature, with a duration ranging from 3 hours to 8 hours depending on the temperature (Table 3)

The reproducibility was evaluated and each isothermal TGA curve was carried out three times.

Table 3: Duration of isotherm at different temperatures

Temperature (°C)	Isotherm Duration (hours)	
	Maritime Pine	Beech
160	24	-
180	24	40
200	16	12
210	9	10
220	5	5
230	5	5
240	3	3
250	3	3
260	3	3

RESULTS AND DISCUSSION

Presentation of TGG curves and choice of a reference temperature T_{ref}

The TGA isotherm of beech at 180°C shows no weight loss during three hours (Figure 2). At 160°C and 180°C, the maritime pine isotherms exhibit a loss of weight during the first 20 min. Above 20 min, their weight is constant. Moreover, isotherms at 160°C and 180°C are superposed. We suggest that the weight loss at the beginning of the isotherm corresponds to resin evaporation. Since the weight stabilises, it also suggests that no degradation of wood constituents occurs at this temperature.

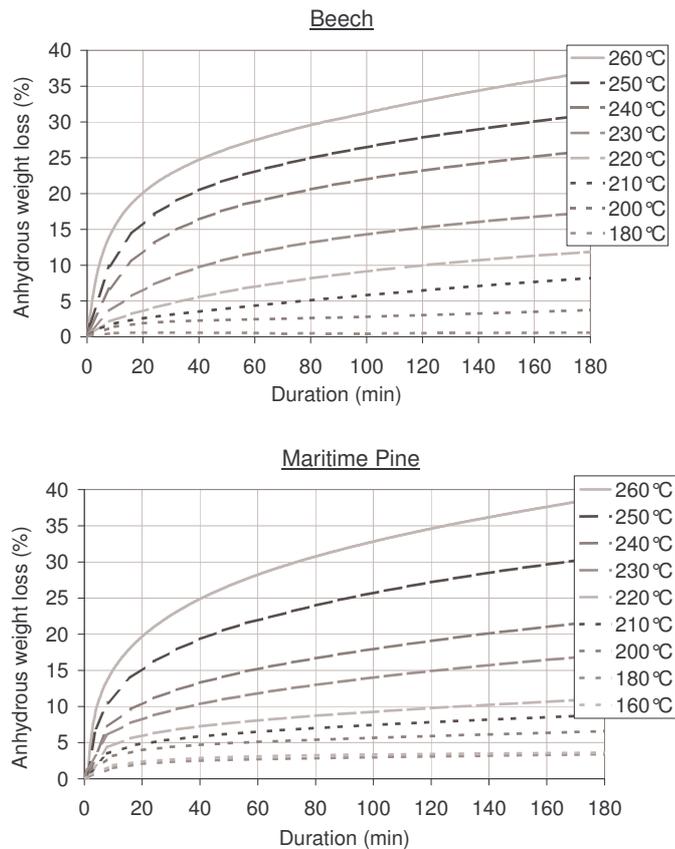


Figure 2: TGA of beech and maritime pine wood.

At 200°C, both beech wood and pine wood lose weight. This loss of weight increases when the duration increases, and should thus be due to wood degradation by pyrolysis reactions. Since 200°C is the lowest temperature at which degradations seem to happen, we chose it as the reference temperature (T_{ref}).

TTE during the first 30 minutes

The DTG curves are presented versus the decimal logarithm of time (Figure 3), in order to check the TTE principle.

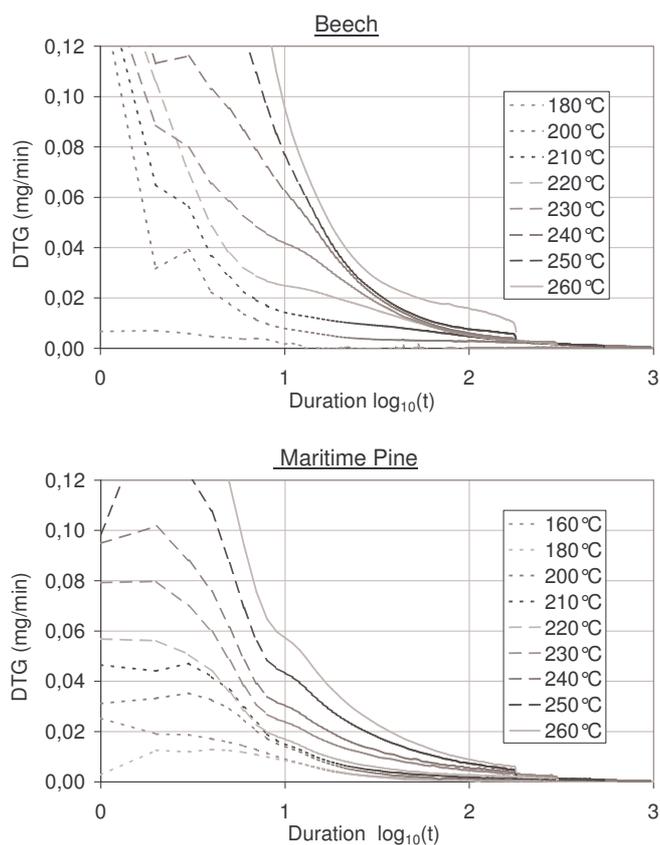


Figure 3: DTG of beech and maritime pine wood

On these two graphs (Figure 3), the TTE principle is verified when the DTG curves can be superposed on each other by a horizontal translation. The first 3 first minutes are unstable and are not discussed.

For maritime pine, it is obvious that TTE is not verified all over the temperature range studied. For a given rate of weight loss, the slope of the DTG curves varies with increasing temperature. This is well visible on maritime pine DTG curves, and less visible for beech wood.

The beech seems to be less resistant and stable than maritime pine at the beginning of the isotherm. Its rate of weight loss is higher than the rate of weight loss of maritime pine; in addition, beech wood DTG's seem to be scattered in the first minutes of isotherm. Consequently, it is not easy to assess if the TTE principle is confirmed or not for beech.

Nevertheless, for beech and maritime pine, superposition of isotherms at 210 and 220°C on the isotherm at 200°C by horizontal translation

seems to be possible. During the first half hour, for maritime pine as well as for beech, the TTE seems to be verified from 200°C to 220°C, and not verified for temperatures higher than, or equal to 230°C.

TTE for durations greater than 30 minutes

It is not possible to see if the TTE is confirmed after 30 minutes (Figure 3). That is why, we calculated t/t_{Tref} (Eqn. 1). According to Equations 2 and 3, when the TTE is verified $\ln(\alpha_T)$ (and consequently t/t_{Tref}) is constant versus R , and should depend only on the temperature.

Figure 4 shows t/t_{Tref} at different values of R and of the temperature of isotherm. when it is constant versus R , it can be concluded that the TTE principle is confirmed. When it is not constant, the TTE principle is not valid.

Concerning beech wood, it is impossible to give any conclusion concerning the TTE principle. The values of $1/\alpha_T$, are too scattered to see if it is constant as a function of R . We suggest that it is a consequence of hardwood thermal instability, which is known to be higher than the thermal instability of softwood.

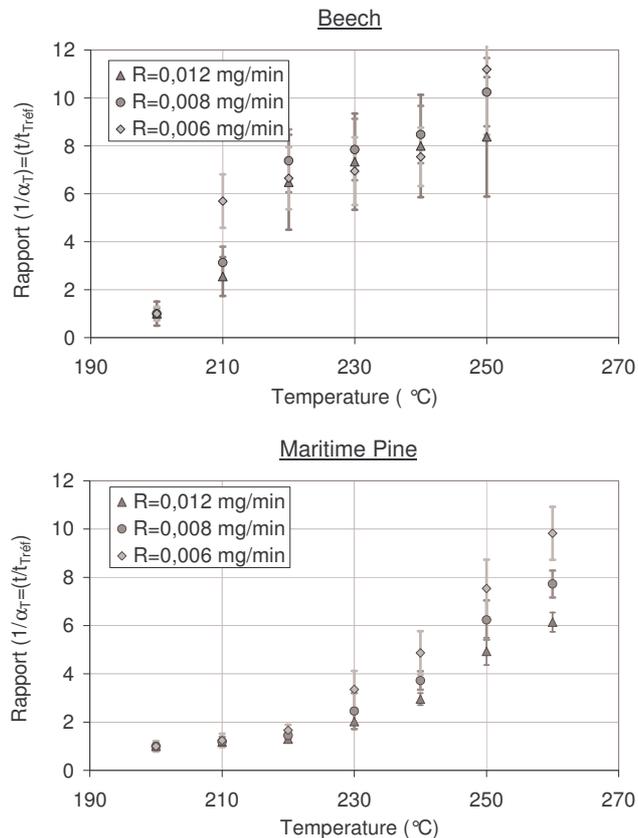


Figure 4: $1/\alpha_T$ in function of temperature, for different values of R .

Concerning maritime Pine, t/t_{Tref} is almost constant versus R at 210°C and 220°C. It increases with R at any temperature higher than or equal to 230°C. This increase is enhanced with temperature augmentation. This observation suggests that for maritime pine, TTE is almost confirmed between 200 and 220°C, and is not verified at temperatures greater than 230°C. Moreover, as the difference of temperature with

reference temperature increases, the TTE principle becomes less applicable.

CONCLUSIONS

Time and duration of heat treatment are crucial parameters to obtain a material with good properties. In this study a methodology (the TTE principle) is adapted from the study of wood viscoelastic properties. It is applied to beech and maritime pine wood powder in order to assess the possibility to optimise treatment time and duration.

Isothermal DTG were analysed according to this TTE principle. It gave relevant results for maritime pine, but not for beech wood. We suggest that it is a consequence of the lower thermal stability of hardwoods compared with softwoods.

For temperatures ranging between 200°C and 220°C, the TTE principle seems to be confirmed for maritime pine. The temperature can be thus increased until 220°C without further loss of mechanical strength. This is not the case for temperatures higher than 230°C, where reactions that favour mechanical strength loss should be enhanced.

An optimisation of heat treatment parameters is thus possible for maritime pine wood. At first, the temperature of treatment should not exceed 220°C. Secondly, in the range of temperature from 200°C to 220°C, the duration has to be increased until the material reaches a certain anhydrous weight loss.

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INVESTIGATION OF THE REASONS FOR THE INCREASE OF WOOD DURABILITY AFTER HEAT TREATMENT BASED ON CHANGES OF WETTABILITY AND CHEMICAL COMPOSITION

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Keywords: Chemical composition, extractives, heat treatment, thermal degradation, wettability, wood

ABSTRACT

Heat treatment of beech wood has been performed at different temperatures to investigate the reasons of its durability increase toward wood rotting fungi. Durability of treated and untreated samples with or without extracts has been estimated using *Coriolus versicolor* on malt agar medium. Relationships between durability and hydrophobicity has been estimated using contact angles measurements, while effects of chemical composition has been undertaken using ¹³C MAS NMR and FTIR analysis and gravimetric measurements. All the results obtained indicated that the hydrophobicity of wood and the extractives generated during heating are not at the origin of the improvement of wood resistance against *Coriolus versicolor*. The most valuable explanation lies in the important changes of wood chemical composition due to hemicelluloses degradation and lignin polymeric network modifications. These chemical modifications allows to explain the higher resistance of modified lignin polymer to fungal enzymes involved in wood degradation, while hemicelluloses, which are generally considered as an important nutritive source for fungi, are already degraded after thermal treatment.

INTRODUCTION

Beech is an important European soft wood species widely used in wood industry. However, its natural durability is too low for hazard class III justifying the recourse to biocides for outdoor applications. Conventional wood preservation systems involve generally impregnation of broadly active biocides into the wood (Barnes and Murphy 1995). However, these techniques generate important environmental hazards, which may limit their scope of applications in the future (Suttie 1997). Furthermore, the increasing environmental pressures appeared since these last years in many European countries led to an important change in the field of wood preservation particularly in regard to the biocides toxicity leading to the development of non biocidal alternatives. Among these alternatives, wood heat treatment, has been intensively investigated to increase durability and service life of non naturally durable species leading to industrial applications (Patzelt *et al.* 2002, Militz 2002). Contrary to the common wood preservation methods, durability does not result only from fungicidal activity but from the change of wood basic properties. According to the literature (Weiland and Guyonnet 2003, Kamden *et al.* 2002), 4 main reasons can be invoked to explain the improved durability of heat treated wood:

- increase of the hydrophobic character of wood, which reduces the sorption of water limiting the growth of fungi.
- generation of new extractives during heat treatment which can act as fungicides.
- modification of the wood polymers leading to a non recognition of these latter by enzymes involved in fungal degradation.
- important degradation of the hemicelluloses, which are generally considered as one of the main nutritive source for fungi.

The aim of this paper is to investigate the effect of heat treatment on wood durability and to bring some evidences on the reasons of its improved durability.

EXPERIMENTAL

Material

Beech (*Fagus sylvatica*) was used throughout this study. Wood samples (blocks or sawdust) were oven-dried at 80°C until stabilization of their mass (approximately 48 hours) before determination of their anhydrous weights.

Heat-Treatment

Heat-treatment was performed on wood blocks (20 x 10 x 30 mm³ in tangential, radial and longitudinal directions) in a reactor placed in an oven at different temperatures during 8 hours under a nitrogen atmosphere. The oven temperature was increased by 20°C min⁻¹ from ambient to the operating temperature. After treatment, the temperature decreases automatically until 20°C. Mass loss was calculated according to the formula (Eqn. 1):

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

Where: m_0 is the initial oven dried mass of wood sample and m_1 the oven dried mass of the same sample after heat-treatment.

Evolution of extractives during heating

Extractives quantities before and after heat treatment were estimated by gravimetric measurements after extraction. The extraction was performed on sawdust obtained after milling of the blocks by two consecutive extractions of 100 min with an ASE 200 Dionex extractor (35 bar) using hexane followed by toluene/ethanol mixture (2/1, v/v) as solvents. Extractives mass was determined after evaporation of the solvent under vacuum and weighing. In the same time, extractions were also performed on blocks using the same procedure to evaluate effect of extractives on decay resistance (m_2).

Contact angle measurements

Wood wettability was measured by the Wilhelmy method according to a reported procedure (Pétrissans *et al.* 2003, Wålinder and Johansson 2001, Wålinder and Ström 2001). Wood plates (20 x 10 x 1 mm³ in

tangential, radial and longitudinal directions) used for θ_a determination were obtained by mechanical sawing. The measuring unit (tensiometer, processor K12 Krüss society) consists of a force measuring system (precision 0.02 mN m⁻¹), a platform drive system to raise and lower the sample automatically and determine its immersion depth during a test cycle. All measurements were performed at 20°C and about 50-60 % relative humidity. The wood sample was immersed in water along the radial direction. The velocity of immersion was 6 mm m⁻¹. Each measurement is repeated four times and averaged.

FTIR analysis

FTIR spectra were recorded as KBr disks on a Perkin Elmer FTIR spectrometer SPECTRUM 2000 at a wavenumber range of 4000-400 cm⁻¹. Finely divided 9 mg wood samples, obtained after grinding of blocks and drying at 80°C, were dispersed in a matrix of KBr (300 mg) and pressed to form pellets. Due to the difficulty to define a reference spectral band, which remains completely invariable, to perform quantitative measurements, all comparisons were made qualitatively.

CP/MAS ¹³C NMR analysis

Solid state CP/MAS (cross-polarisation/magic angle spinning) ¹³C NMR spectra were recorded on a Brüker 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 were 5 KHz. Chemical shifts are expressed in parts per million.

Exposure to Coriolus versicolor

Extracted or unextracted dried blocks (20 x 10 x 30 mm³ in tangential, radial and longitudinal directions) were used for fungal durability evaluations. Petri dishes (9 cm diameter) were filled with sterile culture medium (20 ml) prepared from malt (20 g) and agar (40 g) in distilled water (Gosselink *et al.* 2004), inoculated with *Coriolus versicolor* and incubated at 22°C and 70 % RH to allow colonisation of the medium by the mycelium. Extracted or unextracted blocks (3 replicates) were placed in separate Petri dishes and exposed to fungus during 16 weeks to evaluate influence of the treatment and of the extractives on durability. Each experiment was duplicated. After this period, mycelia were removed and the blocks were dried at 80°C and weighed (m_3) to determine the mass loss caused by the fungal attack (Eqn. 2).

$$ML (\%) = 100 \times (m - m_3) / m \quad (2)$$

Where: m is the initial oven dried mass of wood block before attack (m_0 for controls, m_1 for heat treated blocks and m_2 for extracted heat treated blocks) and m_3 is the oven dried mass after attack.

RESULTS AND DISCUSSION

Weight losses after 16 weeks exposure to *Coriolus versicolor* are reported in Fig. 1. Extracted and unextracted blocks present important weight losses for treatments performed at low temperatures below 180°C. Durability of blocks treated at temperatures above 180°C increases considerably and for blocks treated at 280°C a total inhibition of fungal degradation is observed. In the first part of the curves, weight

losses observed for extracted blocks are generally higher than those observed for unextracted ones certainly due to the presence of natural extracts having some protective effects. For higher treatment temperatures (>200°C), durability of all the blocks increase significantly. No noticeable difference can be observed between extracted and unextracted samples indicating that generation of extractives during heating had no effect on wood decay resistance. Consequently, it's possible to conclude that extracts generated during heat treatment have no effect on the durability. The same conclusions have been made by Kamdem *et al.* (2002) who observed that industrial heat treated pine, spruce and poplar extracted or not with water, acetone or chloroform presented similar weight losses after exposure to different brown rot or white rot fungi.

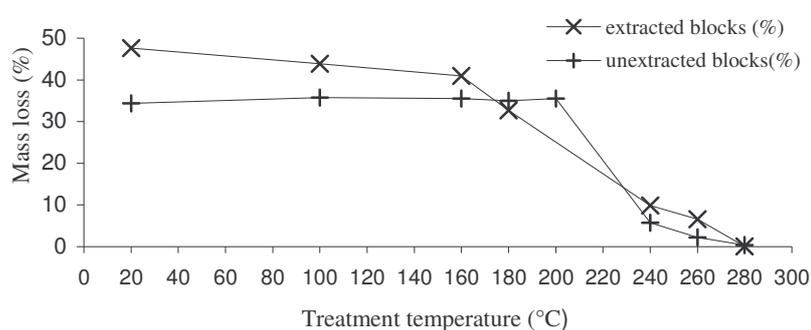


Figure 1: Mass losses of heat-treated beech blocks exposed to *Coriolus versicolor*

Effect of the increase of hydrophobic properties of wood after heat treatment, was investigated using contact angle measurements. Advancing contact angle measured for each wood sample are presented in Figure 2.

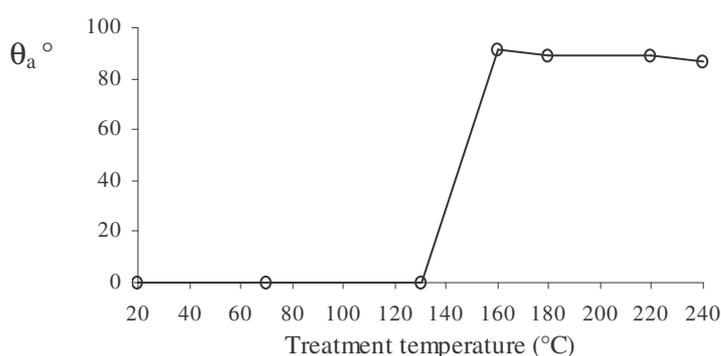


Figure 2: Contact angle evolution during beech heat treatment

For heat treatments below 130°C, the wood remains totally hydrophilic with a θ_a value near from zero. After this temperature, the contact angle value changes rapidly to reach 90° for a treatment temperature between 120 and 160°C. For higher treatment temperatures, the contact angle remains constant and equal to 90°. The beech wood, naturally hydrophilic, becomes rather hydrophobic. For higher treatment

temperatures wood keeps its hydrophobic character with a θ_a value of 90° confirming similar observations reported in a previous study (Pétrissans *et al.* 2003) using industrial heat treated wood. The correlations between wettability and durability are not clear. Indeed, the hydrophobic character, which appears at 160°C and which limits the sorption of water in the wood, have no influence on wood durability. Fungal degradation remains important for blocks treated at temperatures comprised between 160 to 200°C , even if these latter one present no water affinity. According to these results, the hypothesis, concerning the relation between hydrophobic character of wood and growth of fungi, cannot be retained. Similar observations have also been reported by Kamdem *et al.* (2002) who reported that lower moisture content measured in wood after heat treatment are not connected to higher durability to fungi. Gosselink *et al.* (2004) reported also that even if the water uptake of carbonised wood is lower than that of untreated wood when conditioned at 50 or 90% RH, the values obtained by immersion in water are quite similar, which lets to suppose that wood moisture content on malt agar medium are likely to be similar.

Evaluation of the effect of wood chemical composition modification during treatment on its durability was investigated using different approaches. Figure 3 reports the effects of temperature on extracts generation and on wood degradation measured by mass losses of the blocks after treatments.

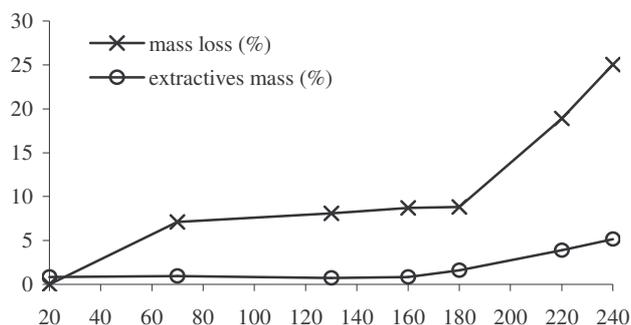


Figure 3: Mass losses and extractives generation during beech heat treatment

Mass evolution starts by a loss of approximately 7 % corresponding to the wood drying phase. Any noticeable mass evolution was observed for temperatures between 80 and 200°C , while, when the temperature becomes superior to 200°C weight losses increase progressively to reach 25 % at 240°C . According to literature, this behaviour can be attributed to hemicelluloses degradation (Weiland and Guyonnet 2003, Weiland *et al.* 1998, Alen *et al.* 2002). From these results, a clear correlation appears between the level of degradation and the beginning of durability improvement. The appearance of new extractives resulting from wood degradation able to possess fungicidal properties does not seem again to have influence on wood durability.

Figure 4 reports NMR spectra of wood samples treated at different temperatures. Solid state NMR measurements have been frequently used to determine chemical modification of polymeric wood

components after heat treatments (Tjeerdsma *et al.* 1998, Sivonen *et al.* 2002). Evolution of NMR spectra recorded at different temperatures indicates that the main modifications appear at temperatures higher than 200°C. Deterioration of hemicelluloses is particularly obvious at 260°C. The shoulder at 102 ppm on the C-1 signal of cellulose at 105 ppm strongly decrease after heat treatment indicating degradations confirming mass losses previously observed at this temperature. The signal of the methyl of the acetyl groups at 20 ppm disappears totally after heat treatment. Changes in the lignin signals are less significant indicating its higher stability. The appearance of signals around 125 to 135 ppm after heat treatment, especially after heating at 260°C, indicates reticulation reactions, like electrophilic aromatic substitutions, on the aromatic nuclei.

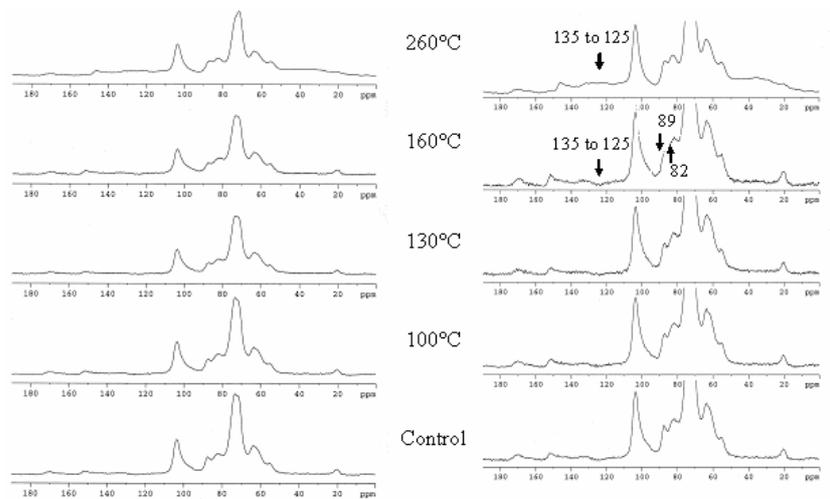


Figure 4: CP/MAS ^{13}C NMR spectra of heat treated beech at different temperatures

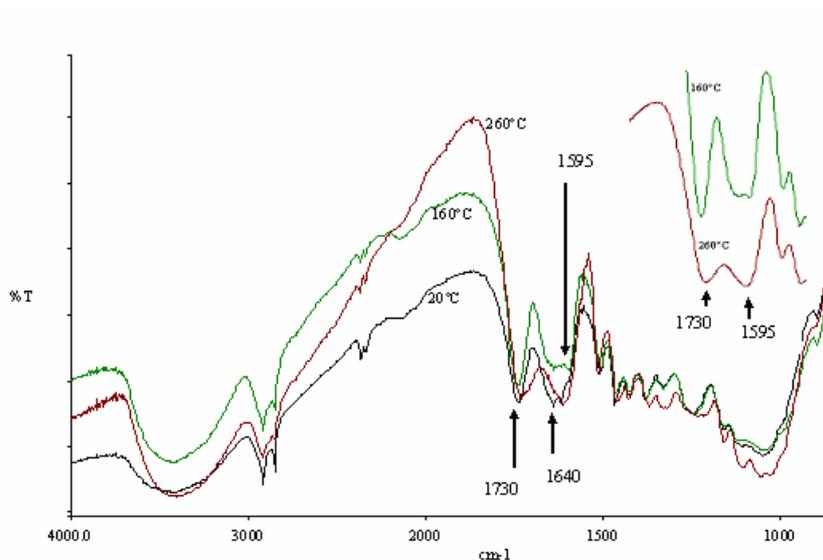


Figure 5: FTIR spectra of heat treated beech at different temperatures

The overall FTIR spectra of both treated and untreated samples indicate that a number of spectral modifications appeared after heat treatment

even if the general aspect of the spectra remains unchanged. The diminution of the water IR absorption band at 1640 cm^{-1} compared to the C=C skeletal vibration band observed at 1595 cm^{-1} confirms the drying phase previously observed. Comparatively to the aromatic band at 1595 cm^{-1} , heat treatment at 260°C leads to a slight decrease of the carbonyl band at 1730 cm^{-1} indicating hemicelluloses degradation. Decrease of the 1465 cm^{-1} band characteristic of lignin C-H vibration confirms the results previously observed by NMR concerning the thermo-condensation of lignin *via* aromatic electrophilic substitutions of aromatic nuclei (Fig. 6).

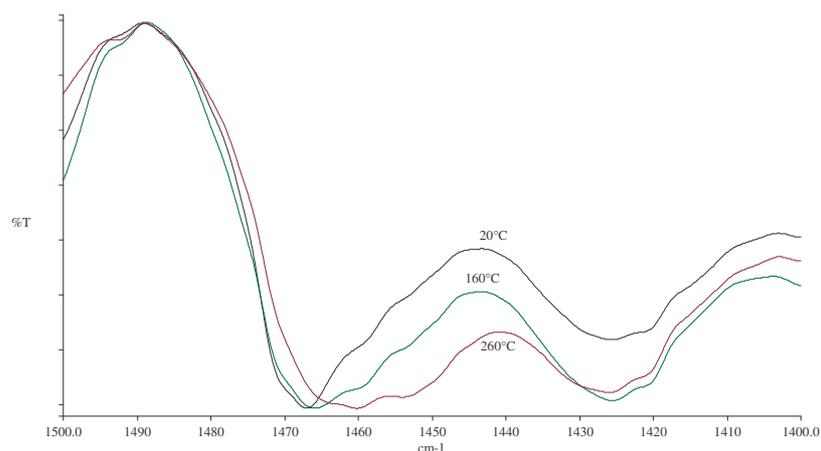


Figure 6: The $1400\text{-}1500\text{ cm}^{-1}$ region of FTIR spectra showing the effect of heat treatment temperature on thermo-reticulation of lignin

According to all these spectroscopic analysis, it seems that hemicelluloses degradation is the most valuable hypothesis to explain the increase of wood durability after treatment at elevated temperature. However, the fact that the white rot fungus, *Coriolus versicolor*, able to degrade lignin and polysaccharidic components of wood, is unable to attack beech wood treated at 260°C indicate that degradation of hemicelluloses is not the only reason involved in the increase of wood durability. Modification of the polymeric network of lignin through reticulation reaction could be also at the origin of these new properties. Further experiments are however necessary to choose between these two hypothesis.

CONCLUSIONS

This study shows that heat-treatment of beech wood increases its durability against the white rot fungus *Coriolus versicolor*. The decay resistance depends of the treatment temperature and is total for treatments performed at 280°C . Wettability changes observed during the heat-treatment do not allow to explain wood enhanced durability, especially for blocks treated between 160 and 200°C , which present an important hydrophobic character but are strongly degraded by *Coriolus versicolor*. In the same time, heat-treated beech wood extracted or not exhibit quite similar mass losses indicating that extractives generated during heating aren't at the origin of wood durability. The important correlation observed between the treatment temperature and the durability, indicates that chemical modifications and degradations,

which have been reported to appear above 200°C in the literature, is the most plausible hypothesis to explain wood durability improvement. In addition to the important degradation of hemicelluloses, which are generally considered as an important nutritive source for the development of wood rotting fungi, modification of lignin network should be also involved to explain the ineffectiveness of fungal peroxidases to degrade lignin.

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A LABORATORY SCALE EVALUATION OF HEAT TREATMENT FOR SOME ASPECTS IN TWO IMPORTANT WOOD SPECIES IN TURKEY

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Keywords: Beech, heat treatment, spruce

ABSTRACT

The exposure of wood to high temperatures has a lot of effects on its properties. These are reduction in hygroscopicity and equilibrium moisture content, improved dimensional stabilisation and biological durability, and a decrease in mechanical properties. Many methods of thermal modification of wood have been reported in the literature. In this study; heat treatment was applied on the spruce and beech wood species which are very important for the wood industry in Turkey. The wood samples obtained from both species were heated in a laboratory scale oven, at four different temperatures (130°C, 150°C, 180°C, 200°C), and three different durations (2 h, 6 h, 10 h) under atmospheric pressure. The performance of heat-treated wood samples was investigated with respect to the physical, mechanical and chemical properties. The general condition of heated wood samples is evaluated, discussed and compared with the literature.

INTRODUCTION

Heat treatment is a process used to modify the properties of wood. Heat-treated wood has been considered as an ecological alternative to preservative impregnated wood materials, and it can also be used for several purposes, *e.g.* for garden, kitchen and sauna furniture, floors, ceilings, inner and outer bricks, doors and windows and for musical instruments (Manninen *et al.* 2002).

Recent work on the heat treatment process of timber to prepare what is currently called torrefied wood in France, Plato wood in the Netherlands and retified wood in the USA, has shown that such types of processes can improve the performance of timber in several respects. Foremost, advantages of wood treated in this manner are its resistance to fungal decay without the need to use chemical preservatives (with consequent environmental advantages) and notably improved water repellency, and improved dimensional stability to moisture variations (Kamdem *et al.* 2000). Many processes of thermal modification of wood have been reported. The main differences between the processes are to be seen in the process conditions (process steps, oxygen or nitrogen, steaming, wet or dry process, use of oils, treatment schedules *etc.*) (Militz 2002). Today, producers co-operate in the research projects, especially those that are concerned with quality control and classification of heat treated wood. The extent of the change in timber properties during heat treatment depends on the maximum temperature and the maximum length of the actual heat treatment period, the temperature gradient, the maximum length of the entire heat treatment, the use and amount of water vapour, the kiln drying process before the actual heat treatment, the wood species and its characteristic properties (Syrjanen and Oy 2001).

In this paper, the physical, mechanical and chemical performance of heat-treated beech and spruce wood (which are two important wood species in Turkey) were studied.

EXPERIMENTAL

Raw materials were (*Fagus orientalis* Lipsky) beech and spruce (*Picea orientalis* (L) Link) woods, obtained from the Black Sea Region in Turkey. Beech and spruce wood were cut in parallel to grain directions and sawn into specimens measuring 2 x 2 x 3 (tangential x radial x longitudinal) cm long for specific gravity and compression experiments. For water repellence and anti swelling efficiency experiments, specimens were sawn into 3 x 3 x 1.5 cm long. For bending strength and modulus of elasticity experiments, specimens were cut into 2 x 2 x 30 cm long. For each wood species and each variation, specimens were stored in 12 treatments groups and for each group, 20 test and 20 control samples were used. The physical and mechanical properties were evaluated according to the Standard Methods of Testing Small Clear Specimens of Timber-ASTM D 143. Conditioning of the samples to 12 % moisture content was done at 21°C and 65 % relative humidity. Heat treatment was then applied on the test samples in an oven which was controlled to a temperature $\pm 1^\circ\text{C}$ sensitively, at four different temperatures (130°C, 150°C, 180°C and 200°C) and three different durations (2, 6 and 10 h) under atmospheric pressure and in the presence of air. Cellulose was determined by the Kurschner-Hoffner's nitric acid method, lignin content was determined as acid-insoluble Klason lignin. Hemicellulose content was found by subtracting cellulose content from holocellulose content. Holocellulose analysis was made according to Wisnes's sodium chlorite method.

RESULTS AND DISCUSSION

Specific gravity, water repellency effectiveness and anti swelling efficiency for two wood species were determined, in order to examine the effects of heat treatment on the physical properties. The results showed that specific gravity values generally exhibited a decrease with increasing exposure temperature and duration, compared to the control groups for both wood species. The highest loss of specific gravity values were obtained from the treatments at 200°C for 10 h for both wood species. The rates of the specific gravity loss in this variation for beech and spruce wood were found to be 17.5 % and 10.5 %, respectively. Fengel (1989) reported that during the heating of ground spruce wood (*Picea abies*) for 24 hours, a loss of weight began at 120°C (0.8 %) and increased to 15.5 % at 200°C. In another study, the thermal treatment of beech wood (*Fagus sylvatica*) with an increasing temperature of 5°C per minute resulted in a loss of weight of 8.1 % at 150°C and of 9.8 % at 200°C. It was recorded that the thermal degradation and formation of volatile products proceeded rapidly when the temperature was elevated above 200°C (Kotilainen 2000). The rate of the weight loss was higher for beech than spruce wood in this present study. According to the earlier researchers; the effects of heat treatment on different wood species are depending on the type and amount of hemicellulose (Giebel 1983, Kollmann and Fengel 1965).

The main effect of heat treatment is a reduction of wood hygroscopicity (Feist and Sell 1987). For this purpose, water repellency effectiveness and

anti swelling efficiency were investigated, which is the best known method of evaluation of the dimensional stabilisation processes of wood (Santos 2000). Water repellency effectiveness and anti swelling efficiency of the samples which were soaked in water for 2, 4, 8, 24, 48, 72 hours and one week, were observed as a result of the different temperatures and durations of heat treatment. It was observed that water repellency effectiveness values generally exhibited an increase with increasing treatment temperature and time and also a decrease after 24 h soaking period almost in all the treatments. The greatest anti swelling efficiency for beech (53 %) and spruce (40 %) wood were obtained from the treatment at 200 °C for 10 h. Related to the wood species and techniques used, the anti swelling efficiency generally are changed between 50 %-80 % (Burmester 1973, Viitaniemi 1997). The obtained results can be explained by the sorption of the chemical wood components cellulose, wood polyoses and lignin and their proportions in the chemical composition of the wood as well as their different thermal stability (Kollman and Schneider 1963).

In most of the publications on the heat treatment of wood, reference is made to improved dimensional stability and increased resistance to fungi, though also to negative changes in the wood's characteristics. The high temperatures during treatment result in a decrease in mechanical properties, an increase of the brittleness and the formation of cracks, in particular (Rapp and Sailer 2001). We investigated the effects of heat treatment on the bending strength of beech and spruce wood. The results showed that there was a linear trend in the decrease in bending strength as time and temperature of treatment increase for both wood species. For the treatment at 200°C, the decrease in bending strength was above 50 % for both wood species. According to some researchers; impact and bending strengths are the wood properties most reduced by thermal degradation (Mitchell 1988). The bending strength can fall by 0-30 %, depending on the treatment conditions (Viitaniemi 1996). Reduction of the strength is dependent on the treatment time, temperature and surrounding atmosphere. In the method developed by the wood material group of VTT Building Technology the treatment is performed in normal pressure, between 180 and 250°C temperatures and by using water vapour as the shielding medium. It was reported that the bending strength is only 14 % lower than that of untreated wood (Viitaniemi 1997).

The effects of the treatment on modulus of elasticity (MOE) of beech and spruce wood samples were observed. The results showed that MOE values generally decreased, especially at higher temperatures and longer durations compared to the control groups, except the treatment at 200°C for 10 h for beech wood. Surprisingly, an increase in MOE of beech wood samples was obtained from the treatment at 200°C for 10 h. The MOE value was greater than the control group and the other test groups. In addition, in the variations heated for long durations at 150°C, 180°C and 200°C for 10 h, the rate of MOE loss was less than the rate for the wood heated over shorter durations. The apparent role of high temperatures and long durations in the increase of MOE can be explained by Hills and Rozsa (1978). They reported that wood is a mixture of polymers of partly crystalline microfibrils and of largely amorphous polymeric hemicelluloses and lignin. It is well known that many amorphous polymeric materials change from their glassy states to rubbery conditions or are capable of large plastic deformation when heated above a certain temperature. At the glass-transition or softening

temperature the individual polymers get sufficient energy to reduce their mutually attractive forces, so that they become rubbery or plastic to a greater degree.

The effects of heat treatment on compression strength were also investigated. The results of the study indicated that the compression strength values of beech and spruce wood samples were reduced with increasing exposure durations and temperatures. The maximum reduction in compression strength (39 %) was obtained from the treatment at 200°C for 10 hours with both wood species. It is known that air atmosphere promotes degradation reactions during thermal treatment. Stamm (1956) demonstrated that the thermal degradation of wood heated in the presence of oxygen is more rapid than that of wood heated in an oxygen-free atmosphere. Rosa and Fortes (1989) reported on the effects of heating cork in air at temperatures in the range of 100 – 300°C. According to them, compression strength is diminished. This change becomes more pronounced with increasing temperature/time.

Changes in the chemical structure of heated beech and spruce wood were examined. The cellulose contents of heat treated wood samples were similar, as compared to each other almost in all treatments or to untreated wood. The cellulose content was between 53 % and 56 %. The treatment was not a cause of degradation of cellulose; furthermore, the cellulose content increased in some treatments compared to control sample (54 %). According to other researchers; the crystalline content of cellulose is not changed (Kotilainen 2000, Runkel and Wilke 1951) or can even increase up to a certain temperature, which may be as high as 200°C depending on the conditions involved. The crystallinity of alkali-resistant cellulose from thermally treated spruce wood increased up to a temperature of 200°C because of a preferred degradation of the less ordered molecules. The annealing of stretched rayon fibers at 200°C initiates a growing of the cellulose crystallites and an increase of the degree of crystallinity (Fengel 1967).

Up to the treatment at 180°C for 6 h, the hemicellulose values were similar as compared to each other or to control sample for beech wood. The lowest hemicellulose contents were found to be 2.38 % and 1.71 % for the treatments at 200°C for 6 h and 200°C for 10 h, respectively while the hemicellulose content of the control sample was 24.66 %. It was observed that the hemicellulose of spruce wood was more susceptible to degradation than the hemicellulose of beech wood. The highest hemicellulose content of spruce wood was 13.67 % (at 130°C, for 2 h) and the lowest hemicellulose content was 1.99 % (at 200°C, for 10 h) while the hemicellulose content of control samples was 21.43 %. Due to the structural heterogeneity of hemicelluloses, it is a complex matter to understand their thermal behavior (Kotilainen 2000, Mannien *et al.* 2002). The lower thermal stability of hemicelluloses compared to cellulose is usually explained by the lack of crystallinity. In addition, more gaseous products and less charred residue are formed in the pyrolysis of hemicelluloses than that of cellulose (Kotilainen 2000).

Up to the treatment at 180°C for 10 h, a linear correlation between increasing temperature and duration of heating and lignin content changing between 20 % - 21 % was not observed for beech wood. For the treatments at 180°C or above and durations longer than 6 h, the lignin content started to increase for each wood species. The highest lignin

content was 42 % for beech wood and 39 % for spruce wood heated at 200°C for 10 h, while the lignin contents of control specimens for beech and spruce wood were 22 % and 24 %, respectively. Kotilainen (2000) reported that, as a general trend, the relative mass proportion of lignin increased with both elevated temperature and extended treatment time, with a simultaneous decrease in the mass proportion of carbohydrates. On the other hand, some of the thermal degradation products of carbohydrates may be retained in the lignin fraction in Klason lignin determination. Though lignin is seen to be the thermally most stable component of wood various changes were observed even at temperatures below 200°C. The determination of the lignin content in thermally treated woods (*Picea abies*, *Pinus sylvestris*, *Quercus robur*) gave evidence of an increase in non-hydrolyzable residue with increasing temperature up to 200°C.

CONCLUSIONS

The results of this study indicated that the decreases in mechanical properties were correlated to the thermal degradation of wood substance and changes of chemical structure of wood components. The decreases in strength properties can be reduced using a closed system with an inert gas such as nitrogen instead of air. Hemicellulose was the most degraded wood-cell component during the heat-treatment. As a component of the wood polymer, hemicelluloses have the main function to connect cellulose and lignin components within the cell-wall substance and also may have “gluing” effects between adjacent cell walls. Thus, changes in, or loss of, hemicellulose due to thermal degradation show some important wood property effects. By this thermal modification, some mechanical properties of wood are reduced, but the most important property of heat treated wood compared to untreated wood is the reduction of the shrinkage and swelling of the wood without using any chemical water repellents. Reduced wood hygroscopicity as the result of blocked hydroxyl groups should have a positive influence on selected wood service properties.

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QUALITY CONTROL OF THERMALLY MODIFIED BALSAM FIR

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Keywords: Acousto-ultrasonic, colourimetry, thermal wood modification

ABSTRACT

This study is investigating the potential of two non destructive methods for quality control of thermally modified Balsam Fir (*Abies balsamea* L. Mill.): colour change with the temperature of treatment (colorimetry) and detection of internal checking (acousto-ultrasonic method). With colorimetry, results indicate that an increase in temperature causes a light blueing for rough wood, a light reddening for planed wood, and a significant decrease of lightness for both. With the acousto-ultrasonic technique, results show a significant decrease of wave propagation time when severe internal checking is present.

INTRODUCTION

Thermal modification of wood changes intrinsic wood properties such as colour, hygroscopicity, durability, dimensional stability, and strength properties. These changes depend on the treatment conditions, where the temperature has a predominant role. In Canada, thermally modified wood is still being produced on a small industrial scale basis only but a growing interest is noted for this new material. No standards of external quality control have been defined so far in this country for thermally modified wood, each treatment plant having their own internal quality control. The development of such standards and quality insurance is a challenging task for the industry, because of the number of treatment processes and species involved.

The aim of this study was to evaluate the potential of two non destructive methods to allow the characterisation of thermally modified Balsam Fir (*Abies balsamea* L. Mill.). These were colorimetry, using the CIE L*a*b* system to follow colour change with temperature of treatment, and the acousto-ultrasonic method using wave propagation time to detect internal checking.

EXPERIMENTAL

Material

Conventionally kiln dried wood boards with nominal dimensions 50 mm x 150 mm x 1200 mm were used for the study. Three temperatures of treatment were applied (185°C, 200°C, and 215°C) with three replications for each temperature, providing nine treatments. These treatments were carried out in an industrial scale reactor using Perdure[®] technology. Thirty specimens were used for each treatment: 15 specimens with narrow annual growth rings and 15 specimens with wide annual growth rings. The 30 specimens were distributed in the

wood load near the bottom and top levels. Thermocouples were used to monitor wood and air temperatures.

Colour measurements

The CIE $L^*a^*b^*$ system is a proven technology for colour measurement. In this system, one colour is measured in a three coordinate space: L^* (Lightness), a^* , and b^* . For each coordinate, there is a pair of colours associated: from white ($L^*= 100$) to black ($L^*= 0$), from red ($a^*= +60$) to green ($a^*= -60$) and from yellow ($b^*= +60$) to blue ($b^*= -60$). The measurements were carried out using a BYK-Gardner Colorimeter with the standard illumination D_{65} which serves for measurements in daylight conditions. On each specimen, 24 measurement points were recorded after heat treatment on rough and planed wood (1 mm on each surface).



Figure 1: Acousto-ultrasonic Apparatus

Acousto-ultrasonic measurements

Acousto-ultrasonic through-transmission was used to obtain wave propagation time. Measurements were made across the width of the board because this direction appears more promising (Niemz and Kucera 1997). The setup consisted of the Sylvatest[®] Duo which includes two piezoelectric transducers, a transmitter and a receiver with conical profile. The transducers were fixed on a sliding support, which allows parallel displacement to the specimen and constant pressure on the contact area with the specimen surface through back springs (Fig. 1). This latter feature made it possible to improve the reproducibility of measurements, since the ultrasonic parameters depend on the pressure applied on the transducers. Wave attenuation measurements were also conducted but results were not found to be consistent.

For this part of the study, the specimens were cut 920 mm long and were planed on all faces to 35 mm thick and 125 mm wide. On each specimen, wave propagation time was measured every 150 mm. At each location along the specimen, the average of three measurements was considered. No measurements were performed close to knots because of their influence on wave propagation. After measurements, the boards were split along the length to determine internal checking and to associate the presence of checking with ultrasonic parameters.

RESULTS AND DISCUSSION

Colour change with treatment temperature

The effect of temperature on wood colour for rough and planed balsam fir is presented in Figs. 2a and 2b, respectively. As reported in the literature, an increase in treatment temperature tends to decrease L^* (Repellin 2002, Bekhta and Niemz 2003). Significant L^* differences for both rough and planed wood were observed. An increase in treatment temperature tends to decrease b^* (blueing) for rough wood and increase a^* (reddening) for planed wood. The latter changes were not perceptible with the naked eye, but trends correspond to those found in literature (Repellin 2002, Bekhta and Niemz 2003). Finally, width of the annual growth rings affected colour measurement of planed wood only.

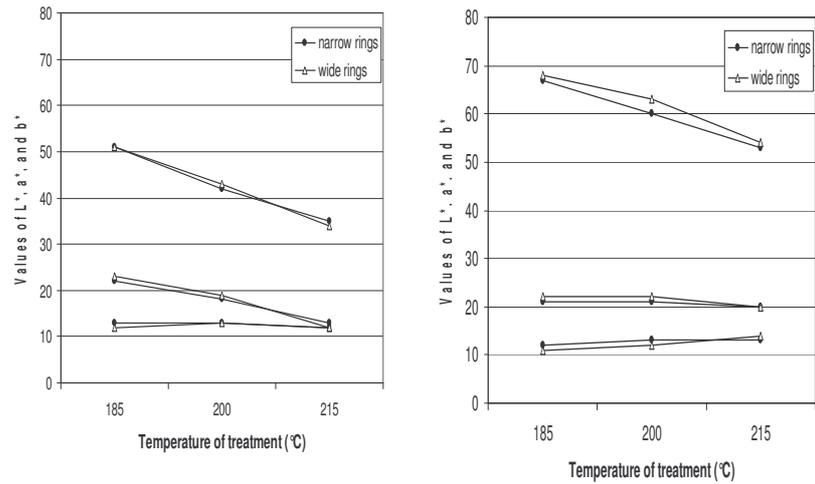


Figure 2: Colour change with temperature for rough (a) and planed (b) wood

Detection of internal checking

For the acousto-ultrasonic measurements, results show a decrease of wave propagation time with internal checking (Table 1). The more severe the checking, the better are the chances to detect it. Values for wood without defects changed for each specimen depending of annual growth rings orientation and width, density, and treatment temperature. Comparison of wave propagation time is then more promising within, rather than between specimens. This conclusion was also reported by Niemz and Kucera (1997) for non-treated wood. Finally, results show that a wave propagation time higher than 175 μ s corresponds to severe internal checking.

Table 1: Comparison of wave propagation time

#	Wave propagation time (μ s)	
	Without defects	With internal checking
1 ^a	131	207
2 ^a	145	178
3 ^a	160	174
4 ^a	148	220
5 ^a	143	187
6 ^a	124	177
7 ^a	173	217
8 ^a	123	184
9 ^a	143	175
Mean (SD)^a	143 \pm 16	191 \pm 18
10 ^b	151	178
11 ^b	148	166
12 ^b	132	135
13 ^b	137	138
14 ^b	150	175
15 ^b	136	177
16 ^b	125	144
17 ^b	134	136
18 ^b	150	169
19 ^b	147	146
Mean (SD)^b	141 \pm 9	156 \pm 18

^aSevere internal checking, ^bLight internal checking

CONCLUSIONS

Increasing the treatment temperature causes a significant decrease of lightness for rough and planed lumber. Significant correlation was also found between temperature and colour attributes b* (blueing) for rough wood and a* (reddening) for planed wood. The width of the annual growth rings affected the colour measurement in the case of planed wood only. The Sylvatest® Duo was adapted to detect internal checking in thermally modified wood. Wave propagation time decreases proportionally with the width of checking. It was not possible to detect very light internal checking.

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COLOUR STABILITY OF THREE DIFFERENT HEAT-TREATED WOOD SPECIES DURING ARTIFICIAL WEATHERING

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Keywords: Heat-treatment, colour change, *Pinus banksiana*, *Pinus strobus*, *Populus tremuloides*

ABSTRACT

This study describes colour stability testing of heat-treated wood samples. Heat treatment was done up to a final temperature of 120°C and of 218°C for jack pine (*Pinus banksiana*), 215°C for trembling aspen (*Populus tremuloides*) and 222°C for white pine (*Pinus strobus*). Heat-treated samples of these woods were exposed to UV-light (QUV equipped with fluorescent lamps UVA-340) for 400 hours with a cycle of 2 hours 30 minutes of radiation at 60°C and 30 minutes of condensation at 40°C. The colour measurements were made at interval of 19, 24, 48, 96, 192 and 400 hours at three different locations on each sample. The results was presented in ΔE and $L^* a^* b^*$ coordinates according to the CIE Lab system. For all samples tested, the discolouration of wood happened mainly during the first hours of accelerated ageing. For the jack pine treated at 120°C and trembling aspen, this discolouration occurred during the first 100 hours of exposure, whereas for jack and white pine, treated at around 220°C, the colour changes was observed in the first 24 hours. After that time, all four kinds of samples showed stability for their colour. Jack and white pine had tendencies to become more red and yellow, whereas trembling aspen become more green and yellow. Darkening of all samples was observed, except for the trembling aspen. Finally, in comparison to their initial states, the jack pine treated at 120°C show the most important colour variation at the end of the accelerated ageing test.

INTRODUCTION

One property of wood is colour change due to exposure of solar radiation. This is mainly due to the short-wave, high energy part of the electromagnetic spectrum that creates chemical changes in the main constituents of wood. Colour change is also influenced by additional factors, such as temperature, water and atmosphere. But, among all environmental factors, UV light is one of the most effective parameter in contributing to the weathering of wood and can penetrate the wood up to 75µm. The penetrating depth depends upon the colour of the original wood. Colour change during exposure is due to modification of all wood components. According to Norrstrom (1969), lignin contributes 80-95 %, carbohydrates 5-20 % and extractives about 2 % to the total UV absorption coefficient of wood. Lignin is the main constituent of wood that absorbs between 200-400 nm and this is where the absorption of radiation occurs at chromophoric structural elements within the molecular network of lignin. The degradation and changes in wood colour occur through radical reaction. Chromophoric groups in lignin absorb light and induce phenoxy radicals. These radicals react with oxygen to form quinone structures which absorb in the visible region.

Consequently, there is depolymerisation of the chemical structure. For decorative end-use (parquets, panels, furniture, etc.), and exterior joinery protected by clear coatings, the colour stabilisation of the natural wood surface is required. Many ways of chemical protection have been investigated to limit wood photodegradation: coatings, painting, chemical modifications and grafting. Thermal treatment of wood at high temperature should be an ecological way to limit photodegradation. The main goal of this work, is to study the response of different wood species in regard of accelerated ageing and to compare jack pine treated at two different final temperatures.

EXPERIMENTAL

Tests specimens

Three species of wood, from Canada's boreal forest, were studied: Jack pine (*Pinus banksiana*) heated up to 120°C and 218°C, White pine (*Pinus strobes* L) heated at 215°C and Trembling aspen (*Populus tremuloides*) heated at 222 °C. For each specimen, three samples of 12 x 6 x 1 cm³ (longitudinal by radial by tangential) was used. For each specimen, only one board was available and a random sampling was done on each board. The final temperature indicated above was the one of the oven dryer and the final temperature of the wood is unknown.

Weathering tests

Accelerated weathering testing was conducted in a Q-panel QUV weathering tester (Q-panel company, USA) equipped with UVA-340 lamps. Three heat-treated samples of each specimen were exposed to UV light directly at a distance of 5 cm for 400 hours. Each cycle comprised 2 hours 30 minutes of radiation at 60°C followed by 30 minutes of condensation at 40°C.

Colour measurement

The colour of the samples was measured at interval of 19, 24, 48, 96, 192 and 400 hours at three different locations on each sample (top, middle and bottom). The measurements were done with a Datacolour international spectrophotometer. The CIELAB system is characterised by three parameters L*, a*, b*. L* axis represents the lightness, it varies from 100 (white) to zero (black), a* and b* are the chromaticity coordinates. In the diagram CIELAB, +a* is the red direction, -a* is green, +b* is yellow, -b* is blue. These values were used to calculate the colour change ΔE^* (Eqn.4) as a function of the weathering time according to the following equations where ΔL_t^* , Δa_t^* and Δb_t^* are the colour changes (Eqn.1, Eqn.2, Eqn.3). Coordinates L*, a* and b* were measured on each sample before accelerated weathering to use them as reference's coordinates.

$$\Delta L_t^* = L_t^* - L_t^* \quad (1)$$

$$\Delta a_t^* = a_t^* - a_t^* \quad (2)$$

$$\Delta b_t^* = b_t^* - b_t^* \quad (3)$$

$$\Delta E_t^* = [(\Delta L_t^*)^2 + (\Delta a_t^*)^2 + (\Delta b_t^*)^2]^{1/2} \quad (4)$$

RESULTS AND DISCUSSION

The most important colour change has been obtained for jack pine heated to 120°C after 400 hours of exposure with a mean ΔE changing from 0 to 30. For jack pine heated at 218°C and exposed for 400 hours the mean ΔE changed only 0 to 4. For trembling aspen and white pine, treated around 220°C, the mean ΔE changed 0 to 9 (Figure 1). All wood samples tested show that colour change occurred mainly during the first hours of accelerated ageing. For the Jack pine treated at 120°C and trembling aspen, the discolouration occurred during the first 100 hours, whereas for jack and white pine (heated ~220°C) during the first 24 h. All samples tested showed a colouration stabilisation (Figure 1). The chromaticity evolution after 400 hours of accelerated ageing showed that jack and white pine became more red and yellow (Table 1) and trembling aspen more green and yellow. Darkening was observed for all samples, except for the trembling aspen.

Table 1: Colour and lightness variation after 400 hours of artificial weathering

Samples	a axis	b axis	L axis
Jack Pine 218°C	Red	Yellow	Lightly darker
Jack Pine 120°C	Red	Yellow	Strongly darker
White Pine	Red	Yellow	Lightly darker
Trembling Aspen	Green	Yellow	Lighten

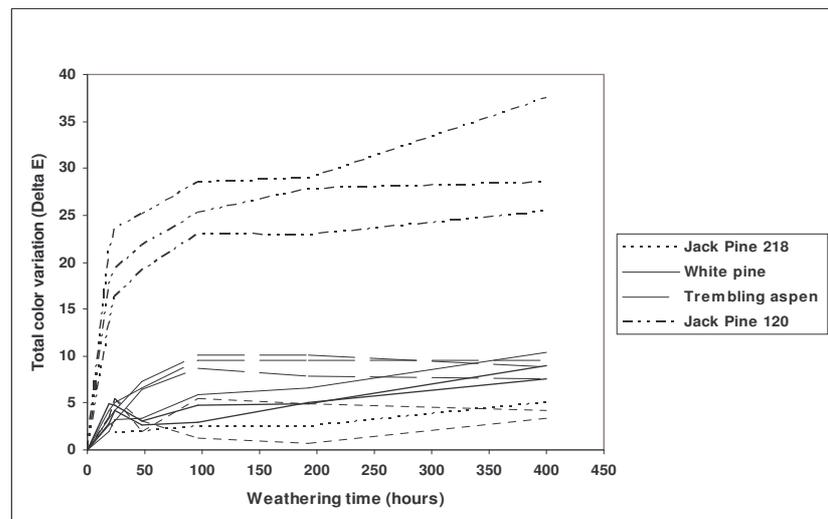


Figure 1: Total colour variation of jack pine treated at 218°C and 120°C, white pine treated at 215°C and trembling aspen treated at 222°C

CONCLUSION

All wood species tested that had been heat-treated over 200°C are less sensitive during artificial weathering, compared to jack pine heated at 120°C. The colour variations occurred during the first 24 to 100 hours before stabilisation. As it was said earlier, the chemical structure of lignin changes during heat-treatment and seems to be less affected by UV light.

Acknowledgements

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RESISTANCE OF THERMO-HYDRO-MECHANICALLY DENSIFIED WOOD TO COLONISATION AND DEGRADATION BY BROWN-ROT FUNGI

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Keywords: Brown-rot, hyphal growth, light microscopy, natural weathering, thermo-hydro-mechanical (THM) wood, wood densification.

ABSTRACT

Colonisation and wood degradation by three brown-rot fungi, *Coniophora puteana*, *Gloeophyllum trabeum* and *Poria placenta* were studied in naturally weathered and non-weathered wood of Norway spruce (*Picea abies*) subjected to three different treatments: hydro-thermal (TH) (160 and 180°C), mechanical densification and thermo-hydro-mechanical (THM) treatment including densification and post treatment under saturated steam conditions at different temperatures (140, 160 and 180°C). The weight loss induced by all three fungi was lowest in THM-densified wood post-treated at 180°C. Highest weight losses were recorded for controls and TH-treated wood. Fungal colonisation varied at its intensity depending on the treatment applied to the wood. Hyphal growth in controls and in TH-treated wood was abundant, whereas in densified and THM-densified wood it was sparse and confined predominantly to the cell lumina of early-wood tracheids. Penetration of large-diameter hyphae and associated degradation in THM-densified wood was impeded by occlusion of the lumina, associated with irreversible compression (loss in shape memory). In contrast to *C. puteana* and *P. placenta*, which showed typical brown-rot behaviour, *G. trabeum* frequently showed hyphal tunnelling within the secondary walls of tracheids and xylem ray parenchyma of controls and thermally treated wood. Such growth was never observed in THM-densified wood post-treated at 180°C.

INTRODUCTION

A process was recently developed for densifying wood by thermo-hydro-mechanical (THM) treatment (Navi and Giradet 2000). The resulting product is several times as dense as the raw material and it shows reduced hygroscopicity, significantly improved mechanical performance and little shape memory (Navi and Giradet 2000). Its resistance to fungal degradation has, however, not been tested.

The purpose of the present study was to test the brown-rot resistance of wood modified by different thermal and densification treatments and to determine whether such resistance is related to patterns of fungal colonisation and cell wall degradation. Naturally weathered and non-weathered wood samples from Norway spruce (*Picea abies*) were used for this purpose and the brown rot fungi used in the study were *Coniophora puteana*, *Gloeophyllum trabeum* and *Poria placenta*.

EXPERIMENTAL

Thermo-Hydro-Mechanical Densification

Wood blocks were obtained from the heartwood of living 40 - 50 yr old trees of *Picea abies* Karst (dimensions 50 x 50 x 150 mm) and subjected to the two-stage THM procedure of Navi and Giradet (2000), involving first densification and then post-treatment in saturated steam at 140°C, 160°C and 180°C. A detailed account of the treatment methods applied is given by Schwarze and Spycher (2005).

Natural weathering

Treated wood blocks were vertically exposed for 12 months on a weathering rack at Empa St. Gallen according to EN 927.

Inoculation of wood blocks

The fungal isolates used for incubation according to EN 113 were: *Coniophora puteana* (Schum.: Fr.) Karst (Isolate-No. Empa 62); *Gloeophyllum trabeum* (Pers.:Fr.) Murrill (Isolate-No. Empa 100); *Poria placenta* (Fr.) Cooke (Isolate-No. Empa 229). The dimensions of the samples after densification were approximately 50 x 25 x 15 mm.

Light microscopy

The incubated test blocks were cut into sub-samples of approx. 20 x 5 x 5 mm, with transverse, radial, and tangential faces exposed for examination. These were fixed in 2 % glutaraldehyde buffered at pH 7.2 - 7.4, dehydrated with acetone and embedded in a methacrylate medium (Schwarze and Spycher 2005). For general observation of cell wall degradation and hyphal growth, sections were stained for 12 h in safranin and then counter-stained for 3 min in methylene blue and for 30 min in auramin.

RESULTS AND DISCUSSION

Densification resulting from wood treatment

THM-treatment, with post-treatment at 140°C, compressed the tracheid lumina to a radial width ranging from 1 to 5 µm in the late-wood and from 1 to 10 µm in the early-wood (Fig. 1). With post-treatment at 160°C, the corresponding values were 0.5 to 2 µm in the late-wood and 1 to 5 µm in the early-wood (Fig. 1). With post-treatment at 180°C, most of the late-wood tracheid lumina were completely occluded, whereas those of early-wood tracheids were reduced to a width of 0.5 to 3 µm (Fig.1).

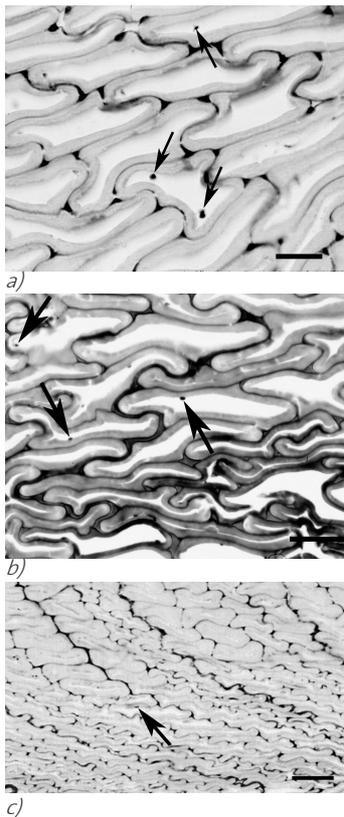


Figure 1: Transverse sections of densified Norway spruce wood; Bar = 10µm. a) Post treated at 140°C, and incubated with *Poria placenta*. Note: Cell lumina of all tracheids are only partially closed. b) Post treated at 160°C and incubated with *Gloeophyllum trabeum*. Note: Both in a) and b) fine hyphae (arrows) are visible within the lumina of early-wood growing on the S_3 . Note for b): cell lumina of some tracheids are completely sealed. c) Post treated at 180°C and incubated with *Gloeophyllum trabeum*. Note: Hyphal growth (arrow) is very sparse and restricted to the early-wood tracheids. Cell lumina of most tracheids are completely sealed.

Fungal colonization and wood degradation

Most test blocks in all the wood treatments were completely colonized by external mycelia after the 16-week incubation period, as assessed by EN 113 criteria. For each fungus, the weight losses were significantly different ($P < 0.05$) amongst the pre-incubation wood treatments. For all the fungi, the highest weight losses were observed in untreated and TH-treated (160°C and 180°C) wood. The lowest weight losses occurred in THM-densified wood post-treated at 180°C. Naturally weathered samples showed higher weight losses after incubation with *C. puteana* and *G. trabeum* presumably due to the set of weathering effects on the wood surface. The strongest effect of weathering was observed for wood samples incubated with *G. trabeum*.

Microscopical examination of the wood blocks showed that the differences between treatments regarding weight loss could be partly attributed to the restriction of fungal growth by the occlusion of tracheid lumina. In wood subjected to THM-treatment and post-treated at 180°C, fungal hyphae failed to grow in cell types with completely occluded lumina and were confined to the partially occluded lumina of the early-wood tracheids. Complete occlusion of all cell lumina would be needed to prevent brown-rot activity, since degradative substances can diffuse from a single hypha in a cell lumen. However, if a high proportion of lumina are completely occluded, this will clearly restrict fungal ingress overall, sufficiently to explain why the rate of decay was reduced.

Although fungal hyphae were unable to enter fully occluded lumina and showed restricted development when occlusion was almost complete, the species tested in this study were able to produce narrow hyphae, which may enable them to enter cells with partially occluded lumina. It seems likely that, in addition to causing occlusion of cell lumina, densification reduces the size of microvoids within cell walls (Hill and Papadopoulos 2001). If so, the diffusion of fungal enzymes through the walls of densified wood may be retarded. A slow rate of diffusion may explain why tree species with naturally dense and highly lignified wood are relatively resistant to decay (Schwarze and Spycher 2005). This may be particularly important in resistance to brown-rot, which mainly involves the diffusion of degradative substances, rather than the direct erosion of cell walls by fungal hyphae. Apart from the effects of densification on the size of cell lumina and voids within cell wall, TH treatment may affect the suitability of wood as a substrate for fungal growth.

In the present study, the moisture content of TH-treated wood was found to be far below the fibre saturation point by the end of the 16-week incubation period. Thus, no free water was available within the cell lumina, so that conditions for hyphal growth and wood degradation were unfavourable. These conditions were, however, circumvented by *G. trabeum*, which switched its mode of action to hyphal tunnelling within the secondary wall so as to utilize the water that was bound there (Schwarze and Spycher 2005). The relatively rapid degradation of such wood may be explained also because its density is reduced due to the depolymerisation of polysaccharides; this is estimated to amount to approximately 5 - 25% in coniferous wood.

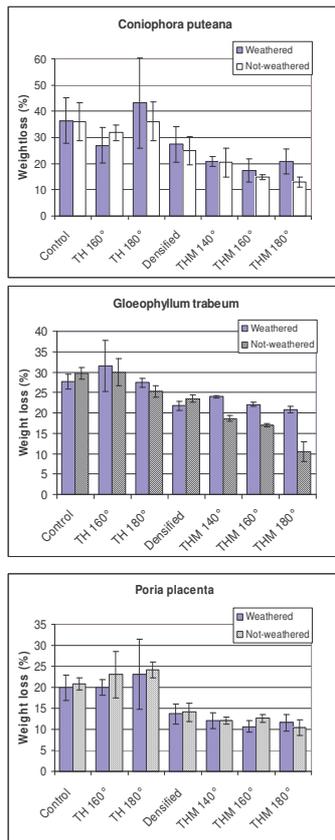


Figure 2: Dry weight losses of wood blocks in untreated controls, TH treated wood (160°C and 180°C), densified wood without thermal treatment and THM densified wood (140°C, 160°C and 180°C) incubated with *Coniophora puteana*, *Gloeophyllum trabeum* and *Poria placenta*. Bars = Standard deviation.

CONCLUSIONS

Post treatment of THM densified wood does not only increase dimensional stability but also appears to induce conditions less conducive to hyphal colonisation of tracheids and xylem ray parenchyma. The extent to which fungal decay is inhibited appears not only to be influenced by chemical but also by physical modifications of the wood structure purely due to occlusion of cell lumina.

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WATER SORPTION PROPERTIES OF THERMO-MODIFIED WOOD

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Keywords: Hydrophilic properties, pine wood, thermal treatment

ABSTRACT

The change in the microstructure and hydrophilic properties of pine wood (*Pinus sylvestris*) due to thermal treatment, namely, hydrothermal (Thermowood Finnforest, temperature 180°C and extra 2 days, 220°C) and in an inert (nitrogen) medium (New Option Wood, temperature 200°C) was investigated by a water vapour sorption method. Based on the measurement of sorption-desorption isotherms in three cycles, the characteristics of the microstructure were determined and the hydrophilic properties of wood, namely, mass (MCC) and surface (SCC) concentrations of hydrophilic centres were characterised. A considerable effect of hydrophobisation (decrease in MCC by 40-55 %, depending on the type and temperature of the treatment) has been established, connected mainly with the inaccessibility of the inner wood surface. After the first sorption-desorption cycle, the hydrophobisation effect decreased 1.5-2 times, after which structure and properties of the samples are stabilised.

INTRODUCTION

During the last decade, several heat treatment methods have been developed. An overview of available technologies and the main material properties is given by Militz (2002). One of the main targets is to modify the wood substrate by the use of elevated temperatures (180°C-220°C) to gain a higher durability against wood rotting organisms and to improve the shrinkage and swelling behavior of wood. At the same time, it is believed that the water vapour behaviour of the wood will be altered. The following research was conducted to gain knowledge on the influence of processes on these properties.

EXPERIMENTAL

Wood samples from different origins were modified by the French company New Option Wood (NOW) and Finnforest (Thermowood) with the following processes:

1. NOW *Pinus sylvestris* (treatment temperature approx. 200°C)
2. Thermowood *Pinus sylvestris* (treatment temperature approx. 180°C)
3. the same material than 3., but with an extra temperature step of 220°C for 48 hours.

Water vapour sorption-desorption isotherms were measured on a vacuum balance with quartz spirals as the sensitive element (sensitivity 1.5-2.0 mm/mg) at the temperature 22 ± 0.1°C. The residual pressure upon vacuum treatment was 1 Pa. The time of reaching the equilibrium in each point of the isotherm was 20 – 24 h. The isotherms were analysed by the comparative method in combination with the BET method (Chirkova 2004). The following characteristics of the samples'

microstructure were determined: accessible specific surface (A , m^2/g), mass concentration of hydrophilic centres a_m , $mMol/g$ (further MMC) and surface concentration of hydrophilic centres α , $groups/nm^2$ (further SMC), with $\alpha = a_m/A$. The pore sizes D were calculated from the Kelvin equation on the basis of desorption isotherms (Gregg and Sing 1982).

RESULTS AND DISCUSSION

Figures 1-3 show isotherms of sorption-desorption of water vapours with the thermo treated wood samples under study, derived in two successive cycles. In all cases of the sorption with thermally treated samples, the sorption of water in the first cycle is much lower than the sorption with untreated wood.

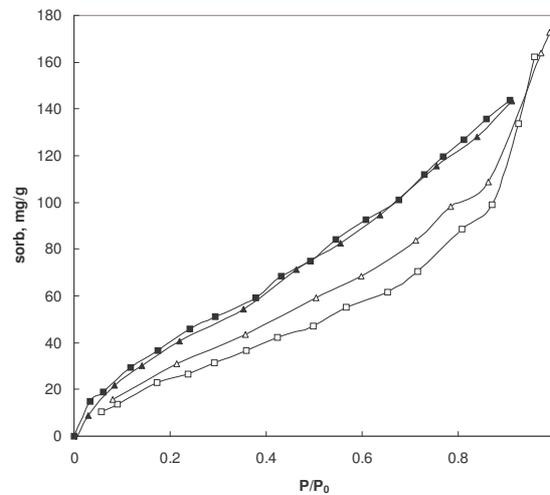


Figure 1: Water vapour sorption-desorption isotherms with the thermo-wood *Pinus sylvestris*, NOW, 200°C. □, ■ - I cycle, △, ▲ - II cycle (empty points – sorption, full points – desorption).

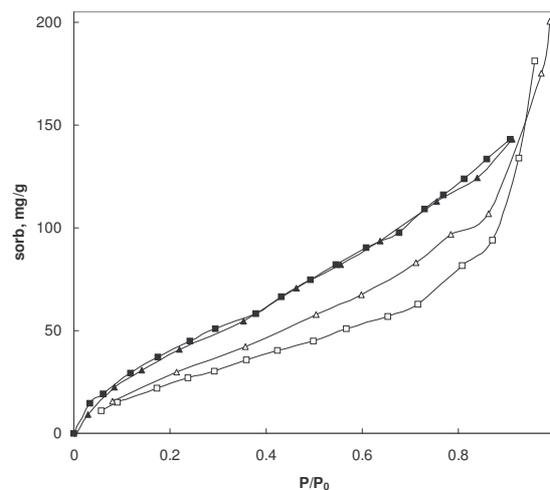


Figure 2: Water vapour sorption-desorption isotherms with the thermo-wood *Pinus sylvestris*, Finnforest, 180°C. □, ■ - I cycle, △, ▲ - II cycle (empty points – sorption, full points – desorption).

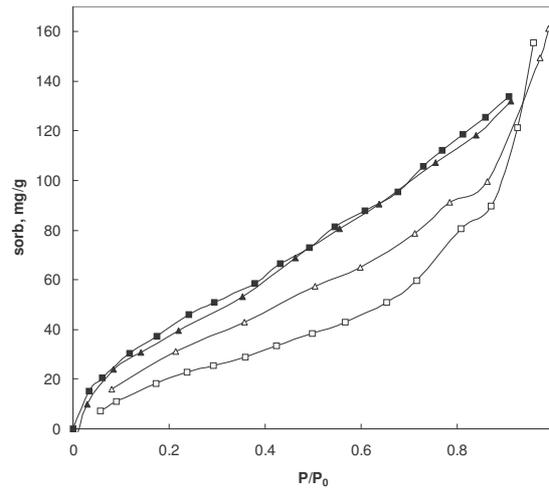


Figure 3: Water vapour sorption-desorption isotherms with the thermo-wood *Pinus sylvestris*, Finnforest, 220°C. □, ■ - I cycle, △, ▲ - II cycle (empty points – sorption, full points – desorption).

Hence, the thermal treatment of wood at the chosen conditions is accompanied by considerable hydrophobisation. The values a_m (MCM), which characterise most completely the hydrophilic properties of the sample, as a result of thermal treatment, decrease by 42-55 % in comparison with untreated wood (depending on the treatment conditions) (Table 1).

Table 1: Structural characteristics of untreated and thermo-treated wood

Sample	Sorption - desorption cycle	A [mz/g]	Change in A [%]	a_m [mMol/g]	Change in a_m [%]	α [groups/nm ²]	Change in α [%]
P.sylvestris untreated	I	320		2.67		5.02	
	II	333	4.0	2.85	6.7	5.16	2.4
	III	342	6.9	2.80	4.9	4.93	1.8
P.sylvestris NOW, 200°C	I	175	45.3	1.56	41.6	5.38	7.2
	II	218	31.9	2.27	15.0	5.80	15.5
	III	236	26.3	2.11	21.0	5.38	7.2
P.sylvestris Finnforest, 180°C	I	165	48.4	1.46	45.3	5.33	6.2
	II	216	32.5	1.83	31.5	5.10	1.6
	III	234	26.9	1.99	25.5	5.12	2.0
P.sylvestris Finnforest, 220°C	I	147	54.1	1.19	55.4	4.87	-3.0
	II	215	32.8	2.18	18.3	6.10	21.5
	III	215	32.8	2.03	24.0	5.68	13.1

However, in the second cycle, after the sorption procedure to the pressure of the saturated vapour and subsequent desorption, the sorption with thermally treated samples increases, and the sorption branches of the isotherms are located higher than in the first cycle. Hence, the structural characteristics of the thermo-treated wood, calculated from the isotherms, change (Table 1). The difference in MCM values between untreated wood and thermally treated samples is equal only to 15-30 %, namely, the hydrophobisation effect in water vapour reduces substantially. At the same time, as can be seen from Figures 1-3,

the desorption branches of the isotherms of the first and second cycles practically coincide, and the sorption isotherms in the third cycle are close to those in the second cycle (not shown in Figure 1). Hence, it may be assumed that, in the first sorption-desorption cycle, the structure of thermally treated wood is stabilised. This is testified also by the values of the structural characteristics calculated from the isotherms of the third cycle (Table 1).

The distinctions in the structural characteristics of untreated and thermally treated wood listed in Table 1 show that the primary effect of hydrophobisation is caused mainly by the decrease of the surface accessible for water molecules, and not by the change in their hydrophilic properties. This is indicated also by wide loops of hysteresis for thermally treated samples in comparison with untreated wood. The decrease of A upon heating up to high temperatures, especially that occurring at a high rate, proceeds owing to the closing of the entries in the cell wall micropores, with the formation of interstructural bonds. At a high humidity (close to the pressure of saturated vapours), these bonds are disrupted, and a greater surface becomes accessible for the sorption of water. Therefore, the sorption in the second cycle grows, and the hysteresis loop narrows. Figure 4 shows the distribution of pore volumes in their sizes for thermo-treated samples. A notable change in the microstructure is observed in the case of treatment at a higher temperature (220°C), namely, the wood becomes microporous and has rather homogenous porosity. This result agrees with the conclusion about the changing in the fractal sizes of wood (from 2.5 to about 3) at high temperatures of treatment (Nakano and Miyazaki 2003).

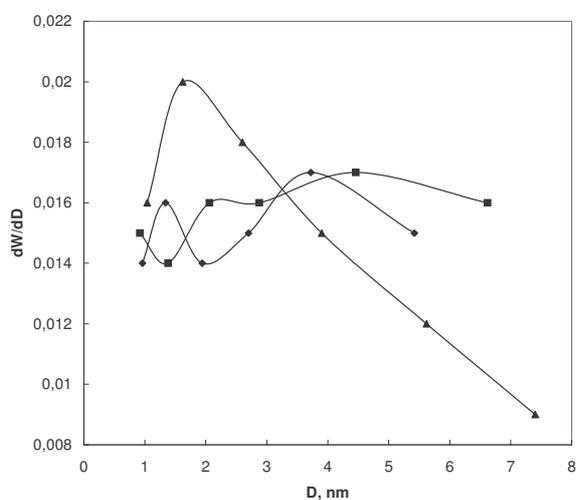


Figure 4: Effective pore size of the thermo-wood samples: \blacklozenge - *Pinus sylvestris*, NOW, 200°C ; \blacksquare - *Pinus sylvestris*, Finnforest, 180°C ; \blacktriangle - *Pinus sylvestris*, Finnforest, 220°C .

A comparison of the three samples under study relative to the hydrophobisation effect shows (Table 1) that the highest effect is reached in the case of the hydrothermal treatment at 220°C , while the sample of hydrothermal treatment at 180°C is most stable. The high enough decrease in MCM of the sample *P. s.* - 220 in the second cycle is connected with the dramatic increase of α upon opening of the surface

in water vapour. The same applies also to the sample *P. s.* – 200 (Table 1). However, the α values of the sample *P. s.*–180 vary little in the process of three sorption cycles, which also confirms its stability. For a more correct comparison of the efficiency of the two methods for thermal treatment applied in the present study, additional investigations in a wider temperature range are necessary. It should be mentioned that, in real conditions of the use of thermo-treated wood, the hydrophobisation effect can be retained for a sufficiently long time owing to the presence of air in wood, hampering the diffusion of moisture.

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THE WATER ABSORPTION OF THERMALLY MODIFIED SAPWOOD AND HEARTWOOD OF SCOTS PINE AND NORWAY SPRUCE

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KEYWORDS: Heartwood, heat-treatment, sapwood, thermal modification, water absorption, wood

ABSTRACT

Water absorption differences between sapwood and heartwood of Scots pine and Norway spruce heat-treated at temperatures of 170°C, 190°C, 210°C and 230°C were investigated. The results were compared to industrially kiln-dried reference samples. Water absorption was determined with a floating test based on the EN 927-5 standard. Generally, the heartwood of both wood species absorbed less water than the sapwood. Heat-treatment evidently decreased the water absorption of spruce and pine heartwood. Pine sapwood quickly absorbed much water, compared to the heartwood of pine. It is very remarkable that heat-treatment at lower temperatures actually increased the water absorption of pine sapwood.

INTRODUCTION

An industrial-scale heat-treatment process of wood, ThermoWood, has been developed in Finland at VTT Building and Transport together with Finnish industry. The ThermoWood process is based on heating the wood material for a few hours at high temperatures over 180°C under normal pressure while protecting it with water vapour. Thermally modified wood is used in several outdoor and indoor applications such as exterior claddings, window and door joinery, garden furniture, decking, floorings, panelling, kitchen furnishing and interiors of bathrooms and saunas.

The chemical and physical properties of wood change during the heat-treatment. The higher the heat-treating temperature and the longer the time, the more significant are these changes. Many earlier experiments show that the wood polymers are degraded, dimensional stability is enhanced, equilibrium moisture content is reduced, colour darkens and biological durability is increased. During the heat-treatment, the wood becomes more brittle and bending and tension strength decrease in relation to the level of heat-treatment. (Viitaniemi 1997a, Jämsä *et al.* 2000, Kamdem *et al.* 2002, Hakkou *et al.* 2005a, Repellin and Guyonnet 2005). Also heat-treatment slows down the water absorption and wettability of wood (Viitaniemi and Jämsä 1996, Viitaniemi 1997b, Pétrissans *et al.* 2003, Hakkou *et al.* 2005b).

Scots pine (*Pinus sylvestris*) and Norway spruce (*Picea abies*) are the main wood species for industrial-scale heat-treatment in Finland. It is well known that with pine and spruce, as with many other wood species, the heartwood has a different chemical composition and physical properties from the sapwood. For example the permeability of heartwood and sapwood have been reported to be different. (Kollmann and Côté 1968)

In this research, water absorption differences between sapwood and heartwood of Scots pine and Norway spruce heat-treated at several temperatures were investigated.

EXPERIMENTAL

Heat-treatments

For the heat-treatments, Scots pine (*Pinus sylvestris*) and Norway spruce (*Picea abies*) planks were selected from a Finnish sawmill. The planks were industrially kiln-dried approximately at a temperature of 70°C to a moisture content of 11-15 %. Half of the planks were sawn from the sapwood part of the logs and half from the heartwood. The planks were heat-treated at VTT under steam at temperatures of 170°C, 190°C, 210°C and 230°C.

Water absorption test

The specimens were sawn from planks heat-treated at VTT. In total, 40 specimens were sawn per each heat-treating temperature (10 replicate specimens of pine sapwood, pine heartwood, spruce sapwood and spruce heartwood). The size of the specimens was 22 x 65 x 150 mm³. The specimens were conditioned at RH 65 % and 20°C to a constant mass. Before the floating test, the specimens were sealed four times at the edges, ends and inner face with impermeable alkyd lacquer. Only the outer faces of the specimens, which were against the water surface in the test, were not painted.

The water absorption test used in the experiments was based on the standard EN 927-5 (2000). After the specimens were sawn, planed, lacquered and conditioned again at RH 65 % and 20°C to a constant mass, they were floated, outer face downwards, in a water basin. The specimens were weighed before the test and again after 3 and 42 days floating. Finally, to calculate the moisture content according to Equation 1, the specimens were dried absolutely and weighed.

$$MC = \frac{(w_{\text{wet}} - w_{\text{dry}}) \times 100\%}{w_{\text{dry}}}, \quad (1)$$

Where w_{wet} = Wet weight of the specimen
 w_{dry} = Dry weight of the specimen

RESULTS AND DISCUSSION

The moisture contents of the specimens during the floating test are presented in Figures 1, 2, 3 and 4. Each column represents the averaged values of ten replicates. Note that the scale of Figure 3 differs from scales in other figures.

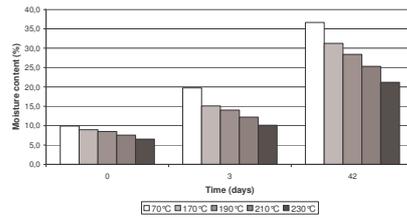


Figure 1: Water absorption of spruce sapwood

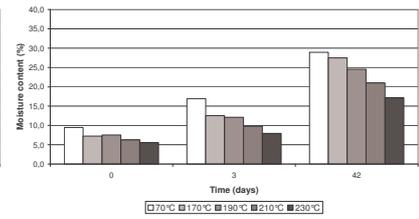


Figure 2: Water absorption of spruce heartwood

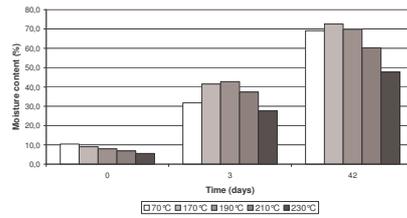


Figure 3: Water absorption of pine sapwood

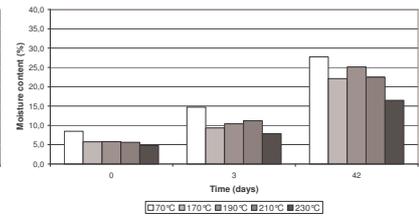


Figure 4: Water absorption of pine heartwood

In general, the water absorption into sapwood was greater than into heartwood with both wood species. This difference was very significant, particularly with pine. The water absorption differences of spruce sapwood and heartwood were significantly smaller than with pine.

The heat-treatment decreased the water absorption of spruce, as was predicted. The reduction of the moisture content of spruce depends on the heat-treatment temperature. The higher the heat-treating temperature, the lower the level of absorbed moisture.

Pine sapwood specimens quickly absorbed much water. Heat-treatment at temperatures of 170°C, 190°C and 210°C increased the water absorption of pine sapwood after 3 days floating. The differences in water absorption of reference samples and thermally modified samples at 170°C and 190°C were smaller after 42 days floating. Heat-treatment at 230°C (floating time 3 and 42 days) and 210°C (floating time 42 days) was effective enough to decrease the water absorption into pine sapwood. Heat-treatment decreased the water absorption into pine heartwood. However, the moisture content after 3 and 42 days floating was not directly comparable with the heat-treatment temperature.

CONCLUSIONS

Very significant water absorption differences between the sapwood and the heartwood of Scots pine and Norway spruce were discovered. Generally, the heartwood of both wood species absorbed less water than sapwood. The differences between sapwood and heartwood of spruce were significantly smaller than with pine. The heat-treatment decreased the water absorption of spruce directly proportional to the heat-treating temperature. In particular, pine sapwood quickly absorbed much water compared to the heartwood of pine. It is very remarkable that unlike with spruce, heat-treatment at lower temperatures actually increased the water absorption of pine sapwood. Heat-treatment decreased the water absorption of pine heartwood.

ACKNOWLEDGEMENTS

Dr Pertti Viitaniemi is gratefully acknowledged for his help and valuable advice. The research was funded by The National Graduate School of Timber Construction in Finland.

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PHYSICAL PROPERTIES OF THERMALLY MODIFIED BALSAM FIR AND JACK PINE

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KEYWORDS: Thermally modified, balsam fir, jack pine, properties

ABSTRACT

Thermally modified wood is defined as wood heated between 160 and 245°C within a controlled oxygen reduced atmosphere. This treatment results in chemical modification of the wood structure. As a result, physical properties of thermally modified wood are different from those of regular wood. For twenty years, many heat treatment processes have been developed in France, Finland and other countries. Industrial production of thermally modified wood has been performed at a small scale in Eastern Canada. However, interest for thermally modified wood products is growing rapidly in Canada. Since 2002, the eastern laboratory of Forintek Canada Corp. has conducted studies on balsam fir and jack pine thermally modified using three different commercially available technologies. Tests results show that wood properties were significantly affected by thermal treatments: while resistance to abrasion, impact bending and MOR decreased, dimensional stability and resistance to fungal decay were improved. MOE was not significantly reduced by heat treatments.

INTRODUCTION

The general objective of the present study is to determine properties of thermally modified wood vs. natural kiln dried wood. Tests were performed on balsam fir and jack pine thermally modified at 210°C by three industrial technologies. Assessed wood properties were resistance to abrasion, dimensional stability, resistance to fungal decay, impact and static bending (MOE and MOR).

EXPERIMENTAL

Material used for high-temperature treatments were kiln dried balsam fir (*Abies balsamea*) and jack pine (*Pinus banksiana*) lumber 50 mm x 150 mm x 2.44 m, premium graded. After treatments, wood was conditioned at 20°C and 40 % RH for two weeks before preparing the required wood samples for each test.

Resistance to abrasion was determined by using a taber abraser with a H-22 abrasive wheel type. Mass loss of 10 mm x 10 mm x 2 mm-thick specimens was measured after each 100 cycles of abrasive wheel, up to 500 cycles. Dimensional stability was determined by measuring mass and dimension of samples after four cycles of 24 h-water immersion followed by 7-days conditioning treatment at 20°C and 20 % RH. Initial dimension of wood samples were 76 mm x 19 mm x 76 cm. Resistance of wood to fungal decay was determined following the AWPA E-10-91 *Standard method of testing wood preservatives by laboratory soil-block cultures*. Fungi used in these tests were the brown-rots *Gloeophyllum trabeum* and *Postia placenta* and the white-rots *Trametes versicolor* and *Irpex lacteus*. Results are presented as weight-loss percentages

after an incubation of 20 weeks. Impact resistance was evaluated based on ASTM D-143 *Standard methods of testing small clear specimens of timber*. Impact bending tests were performed on 50 mm x 50 mm x 760 mm specimens. An impact machine with a 22.5-kg hammer was used with a 1.27-mm increasing drop until complete failure or 150-mm deflection of the specimens occurred. Finally, static bending tests based on ASTM D-143 were performed on 50 mm x 50 mm x 760 mm specimens in order to determine MOE and MOR.

RESULTS AND DISCUSSION

Mass loss of unmodified and thermally modified wood samples of balsam fir and jack pine after 500 cycles of the abrasive wheel are shown in Figure 1. Results show that resistance to abrasion of wood is reduced by thermal treatments. The resistance to abrasion of thermally modified wood vary with the technology used for the treatment.

Figure 2 shows the average width variation of unmodified and thermally modified jack pine samples following each period of 24-h water immersion and 7-days conditioning treatment at 20°C and 20 % RH. Tangential shrinkage and swelling of thermally modified wood is reduced by around 70 %. From Figure 3, resistance to fungal decay of thermally modified jack pine was improved. Unmodified jack pine was mostly affected by brown-rots *Gloeophyllum trabeum* and *Postia placenta*. In these cases, mass loss of jack pine thermally modified by technology 2 was reduced by close to 65 % vs. unmodified wood. Figure 4 shows the impact bending test results as the average height of a 22.5 kg hammer drop resulting in a complete failure or 150-mm deflection of the unmodified and thermally modified balsam fir and jack pine samples. Resistance to impact bending of thermally modified wood is lower than unmodified wood. Results vary with the technology used for high-temperature treatment.

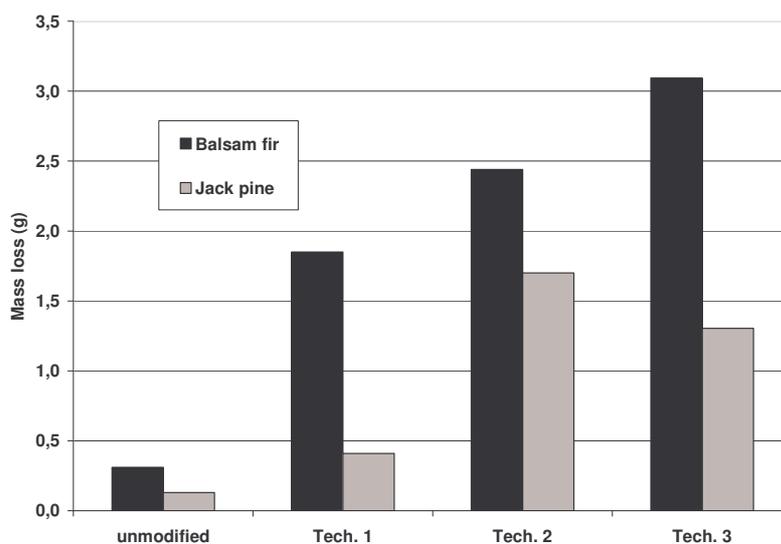


Figure 1: Resistance to abrasion of unmodified and thermally modified balsam fir and jack pine

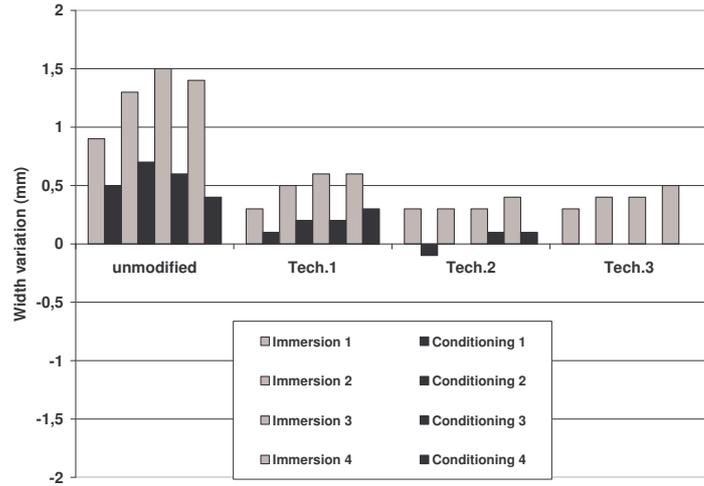


Figure 2: Dimensional stability (width variation) of unmodified and thermally modified jack pine

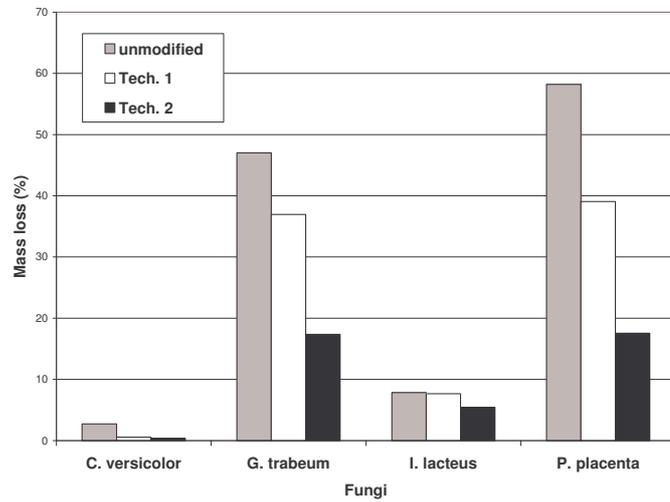


Figure 3: Resistance to fungal decay of unmodified and thermally modified jack pine

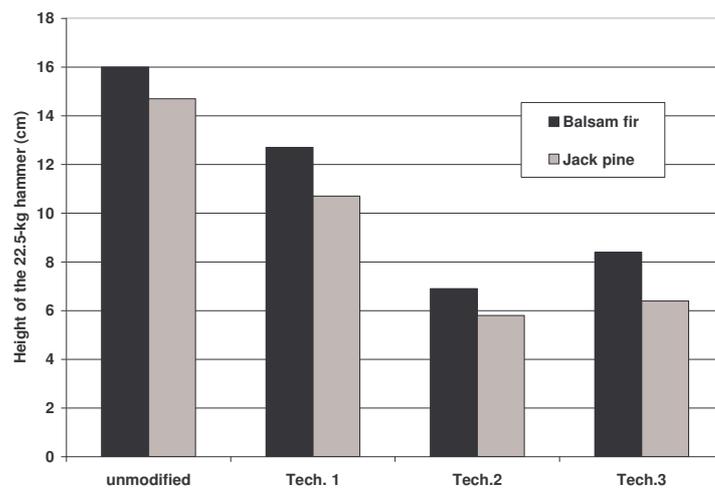


Figure 4: Impact resistance of unmodified and thermally modified balsam fir and jack pine

MOE and MOR values for unmodified and thermally modified balsam fir and jack pine are shown in Figures 5 and 6. Except for balsam fir modified by technology no.3, results show no decrease of MOE values following high-temperature treatment. From Figure 6, MOR values of thermally modified wood decreased after thermal treatments, except for jack pine modified by technology no.1.

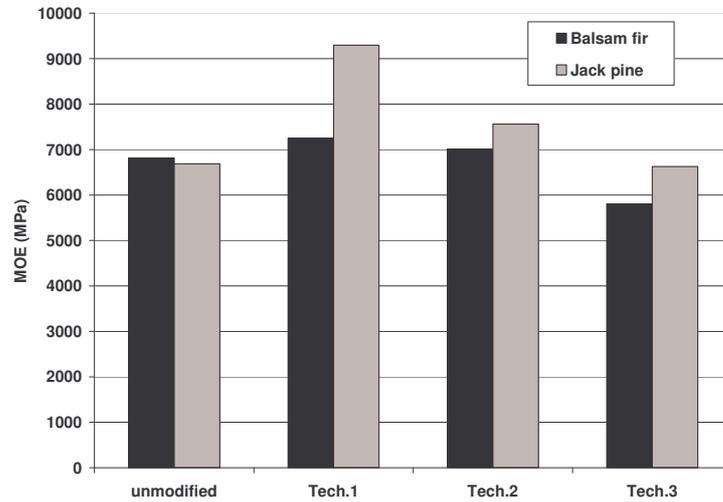


Figure 5: MOE of unmodified and thermally modified balsam fir and jack pine

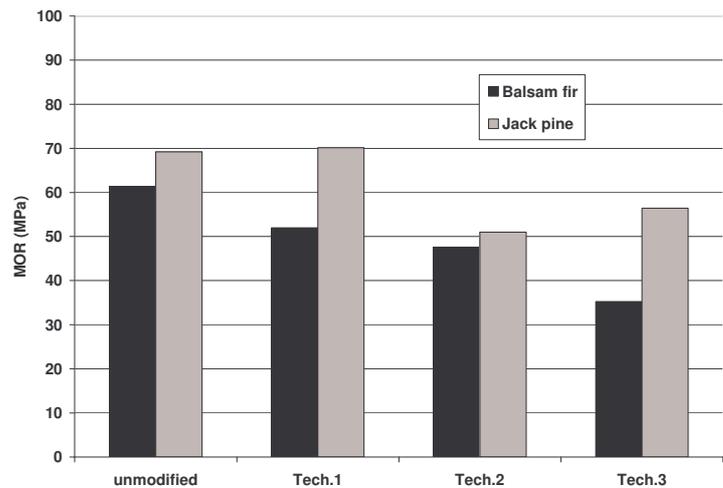


Figure 6: MOR of unmodified and thermally modified balsam fir and jack pine

CONCLUSIONS

Tests results on balsam fir and jack pine show a reduction of resistance to abrasion, impact bending and MOR after thermal treatments. However, dimensional stability and resistance to fungal decay were improved. Finally, results show that MOE was not reduced by thermal treatments.

ACKNOWLEDGEMENTS

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CORROSION OF FASTENERS IN HEAT-TREATED WOOD – PROGRESS REPORT AFTER TWO YEARS' EXPOSURE OUTDOORS

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Keywords: Corrosion, fasteners, heat-treatment, nails, screws, thermal treatment

ABSTRACT

The corrosion of common fastener materials now in use - mild steel, zinc-coated steel, aluminium and Sanbond Z-coated steel – has been evaluated after two years' exposure outdoors in untreated and heat-treated spruce (*Picea abies*) respectively. Spruce from South-western Sweden was used. The heat-treatment was carried out in Finland according to the ThermoWood process at a maximum temperature of 220 °C for five hours. The results so far show that the corrosion of fasteners in heat-treated wood according to the particular specification is more severe than in untreated wood. Mild steel and zinc-coated steel are the most susceptible. Stainless steel has shown the best performance so far.

INTRODUCTION

The properties of the heat-treated wood in interaction with other materials is an important aspect of the performance of a construction of heat-treated wood and its overall durability. The aim of this study was to investigate the effect of heat-treated wood on different types of metal fasteners in comparison with untreated wood. The trial is part of a series of investigations of heat-treated wood that SP Swedish National Testing and Research Institute initiated in 2001 with financial support from the Swedish Wood Association (Jermer *et al*/2003). In this paper, results after two years' exposure outdoors are reported.

EXPERIMENTAL

Material

The fasteners tested are described in Table 1. The areas have been calculated based on the nail and screw dimensions given and are considered as accurate as possible.

Spruce (*Picea abies*) from South-western Sweden was used and the heat-treatment was carried out in Finland according to the ThermoWood process. The maximum temperature of 220 °C was held during five hours.

Table 1: Fasteners in corrosion trial with untreated and heat-treated wood

Type of fastener	Dimensions	Material	Area cm ²	Supplier	
Nail Mild steel	50x2.0 mm	Steel quality CD9 (EN 10016-2)	4	Gunnebo AB	Fastening
Nail Zinc coated steel (hot- dip galvanized)	50x2.0 mm	Steel quality CD9 (EN 10016-2) zinc coating > 50 µm	4	Gunnebo AB	Fastening
Nail Stainless steel	50x2.0 mm	Steel quality A4 (SS 2347)	4	Gunnebo AB	Fastening
Nail Aluminium	50x4.0 mm	Al-wire* (SS 4120)	6.5	Gunnebo AB	Fastening
Screw "Grabber" Sanbond Z-coated steel	42 mm (length)	Steel quality C1018; coating of nickel, zinc and chromate >16 µm	4	Arne Thureson Byggmaterial AB	

*Al 97.2 %, Mg 2.2-2.8 %, Cr+Mn 0.15-0.50 %

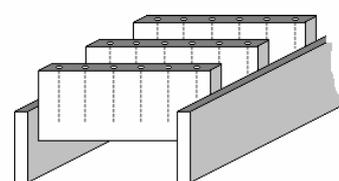


Figure 1: Sample set-up for corrosion testing

Methods

Each fastener was washed in ethanol and then weighed, before being applied to a sample of 45x145x500 mm, standing upright as in Figure 1. The fasteners are thus tangentially oriented in the wood sample. The trial set-up is a modified set-up used by Boliden AB in a trial carried out in the 1970's (Berglund and Wallin 1978). A sealing compound was applied between fasteners of different materials to prevent galvanic elements from arising if water remains on the horizontal surface.

At the first inspection after two years, two fasteners of each kind and each kind of wood were removed, and inspected visually. The rating was done according to Table 2. In addition to the visual inspection the metal loss (corrosion rate) was also calculated.

Table 2: Visual assessment of corrosion attack

Rating	Description	Definition
0	No attack	
1	Insignificant attack	<5 % of surface attacked
2	Slight attack	5-50 % of surface attacked
3	Serious attack	50-95 % of surface attacked
4	Completely attacked	>95 % of surface attacked

Attacks on both surface coating and the basic material were assessed using the same scale. The rating was then weighted using the following formula (Equation 1):

$$\text{Weighted rating} = \frac{\text{rating surface coating} + 3 \cdot \text{rating basic material}}{4} \quad (1)$$

The metal loss was calculated and expressed as metal loss per surface unit (g/m²), and as depth of corrosion (µm).

In order to determine the metal loss and depth of corrosion the corrosion products had to be eliminated. Thus the fasteners were pickled, cleaned and then weighed. Pickling and cleaning were performed as follows:

1. Five minutes pickling in an ultrasonic bath
2. Two minutes cleaning in hot water in an ultrasonic bath

3. Ten seconds rinsing in hot running water
4. Drying with a clean paper tissue
5. Dipping for 30 seconds in 96 % ethanol
6. Drying with a clean paper tissue
7. Storage for at least one hour in a desiccator. To equalize the temperature, this was done in the same room as the weighing.

The pickling solutions used are specified in Table 3.

Table 3: Pickling solutions

Metal/Surface treatment	Temperature, °C	Pickling solution
Steel	25	Clark's solution: Concentrated hydrochloric acid with an additive of 20 g/l antimony oxide and 20 g/l stannic chloride
Aluminium	80	Chromic acid 20 g/l and phosphoric acid 50 ml/l de-ionized water
Zinc-coated and Sanbond Z-coated steel	25	5 % acetic acid in de-ionized water

All fasteners were pickled, with the exception of the stainless steel nails. After pickling the fasteners were weighed and the weight loss calculated as the difference between the original weight (prior to exposure in the trial) and the weight after pickling.

Thus, the metal loss per surface unit was calculated accordingly (Equation 2):

$$\text{Metal loss (g/m}^2\text{)} = \frac{\text{Original weight (g)} - \text{Weight after pickling (g)}}{\text{Fastener area (m}^2\text{)}} \quad (2)$$

The depth of corrosion is another way of expressing the metal loss and means that the thickness of the lost metal layer is calculated according to the following formula (Equation 3):

$$\text{Depth of corrosion (}\mu\text{m)} = \frac{\text{Metal loss (g/m}^2\text{)}}{\text{Density (kg/dm}^3\text{)}} \quad (3)$$

The following densities were used:

Mild steel	7.8 kg/dm ³
Zinc-coated steel	7.1 kg/dm ³
Aluminium	2.7 kg/dm ³
Stainless steel	7.9 kg/dm ³

Results

Figure 2 shows examples of fasteners exposed in heat-treated and untreated wood. The result of the visual inspection is presented in Figure 3. Metal loss and depth of corrosion after two years' exposure are presented in Tables 4 and 5, and in Figure 4 the depth of corrosion is presented graphically.



a)



b)

Figure 2: a) Fasteners exposed in untreated wood. b) Fasteners exposed in heat-treated wood

Result of visual inspection of corrosion of fasteners in heat treated and untreated wood.

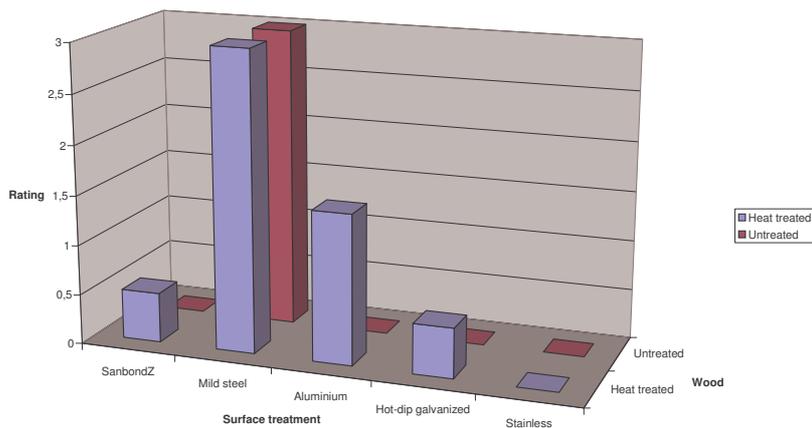


Figure 3: Result of visual inspection of corrosion of fasteners in heat-treated and untreated wood

Table 4: Metal loss (g/m²) of fasteners in heat treated and untreated wood after two years' exposure

Fastener	Nail mild steel	Nail hot-dip galvanized steel	Nail stainless steel	Nail aluminium	Screw steel coated with Sanbond Z
Heat-treated	456	229	0	46	116
Untreated	188	34	0	23	49

Table 5: Depth of corrosion (µm) of fasteners in heat-treated and untreated wood after two years' exposure

Fastener	Nail mild steel	Nail hot-dip galvanized steel	Nail stainless steel	Nail aluminium	Screw steel coated with Sanbond Z
Heat-treated	58	32	0	17	16
Untreated	24	5	0	8	7

Depth of corrosion of fasteners in heat treated and untreated wood after two years' exposure

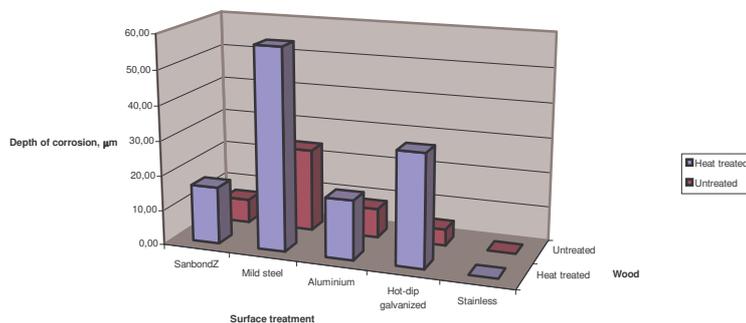


Figure 4: Depth of corrosion (µm) of fasteners in heat-treated and untreated wood after two years' exposure

Stainless steel has performed the best so far, with basically no corrosion at all. Aluminium and Sanbond Z-coated steel has also performed fairly well, whereas mild steel has been severely attacked in the heat-treated

wood. Hot-dip galvanized steel has, surprisingly enough, been moderately attacked in the heat-treated wood already after two years' exposure.

There was a fairly good correlation between the results of the visual assessment and the depth of corrosion. However, the actual corrosion found for hot-dip galvanized steel was more severe than found at the visual inspection.

CONCLUSIONS

Although only two fasteners of each kind have been examined and the time of exposure was only two years, it seems that heat-treated wood is more aggressive to all metals and coatings tested, except for stainless steel, compared with untreated wood. A possible explanation is the existence of residual acids, mainly acetic and formic acids (Bourgois and Guyonnet 1988, Manninen *et al.* 2002, Tjeerdsma *et al.* 1998, Sundqvist 2004), that are formed during the heat treatment. It has to be pointed out that the results from this study may not be valid for heat-treated wood in general but so far only for heat-treated wood treated according to the particular process applied.

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THERMAL MODIFICATION OF NEW ZEALAND RADIATA PINE

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Keywords: Decay resistance, dimensional stability, New Zealand, radiata pine thermal modification

ABSTRACT

A pilot-scale kiln was used to investigate thermal modification of New Zealand radiata pine. The modified timber has improved dimensional stability and reduced equilibrium moisture content. The entire cross section of the wood becomes darker. In-grade stiffness of the modified timber decreases by 10-20%. Strength and toughness of small clear specimens is also reduced. Fungal cellar stakelet tests, accelerated wall framing decay tests and interim long-term outdoor exposure trials indicate improved resistance to decay. Radiata pine is suitable for drying at high temperatures, and can be thermally modified from green in under 25 hours, with minimal distortion and degrade. Thermally modified New Zealand radiata pine would be suitable for claddings, decking, indoor and outdoor furniture, joinery and framing.

INTRODUCTION

Thermal modification decreases the hygroscopicity of wood, which improves stability and fungal resistance. This process has achieved commercial success in Europe with hardwoods and softwoods (Militz 2002). Demand is steadily increasing with growing awareness of the intrinsic benefits of thermally modified wood.

New Zealand radiata pine is a highly permeable, fast-growing, intensively managed softwood, which preliminary research suggests is suited to thermal modification. Radiata pine dries easily at high temperatures, allowing green wood to be dried and modified in one short step. Timber for cladding has been dried, modified and reconditioned in 25 hours without significant distortion or checking.

A 5 m³ Tekmaheat thermal modification kiln, owned by Carter Holt Harvey Ltd. is located at Forest Research in Rotorua, New Zealand. This kiln has been used to; evaluate the properties of radiata pine modified at different temperatures; determine appropriate schedules for modifying radiata pine; and assess the suitability of thermally modified radiata pine for specific end uses. Five treatment temperatures were compared: 170, 190, 200, 210, 230°C. Kiln dried, decking grade timber was sorted to give a similar stiffness distribution in each charge. This paper examines the effect of thermal modification on some physical and mechanical properties of New Zealand radiata pine and discusses a range of potential end uses.

RESULTS AND DISCUSSION

Physical Properties

Thermal modification reduces the equilibrium moisture content (EMC) and increases the dimensional stability of radiata pine. Small samples of thermally modified radiata pine were cycled between 35 and 95 % relative humidity at 25°C. From 35 to 65 % relative humidity, wood modified at 210°C swelled half as much as unmodified kiln dried wood (Figure 1). At 65 % relative humidity, unmodified, kiln dried radiata pine had an EMC of 13 %, whereas radiata pine thermally modified at 210°C had an EMC of 10 % (Figure 2)

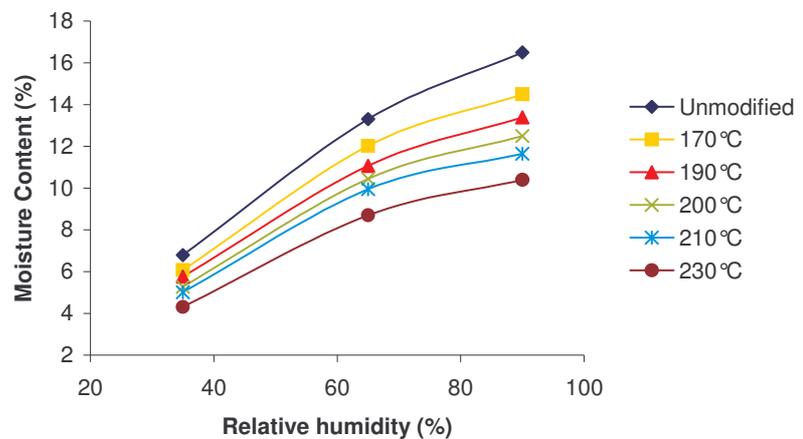


Figure 1: Equilibrium moisture content over 3 humidity cycles, average of adsorption and desorption

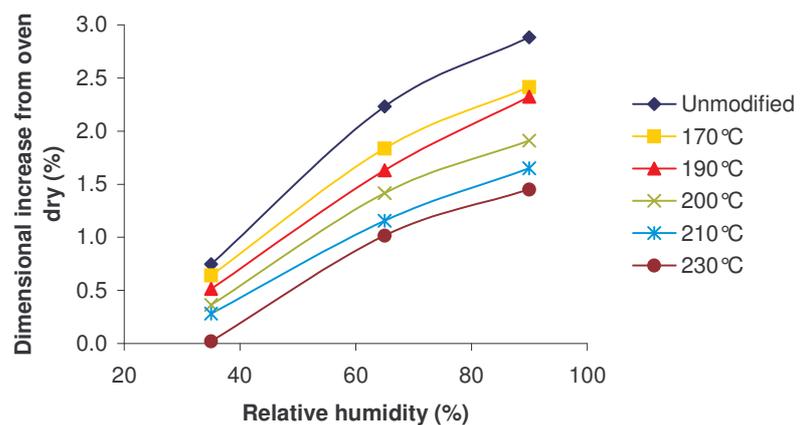


Figure 2: Dimensional stability over 3 humidity cycles. Average of radial and tangential directions, averaged for adsorption and desorption

The reduced hygroscopicity promotes resistance to fungal attack. Radiata pine thermally modified at 230°C has performed similarly to wood treated with Copper Chrome Arsenic (CCA) to hazard level H3 (outside, above ground exposure) during a 12 month fungus cellar trial (Figure 3). The index of condition describes the amount of decay in a sample, 10 indicating no decay and 0 complete decay. Ongoing outdoor exposure indicate an increase in decay resistance with increasing modification temperature.

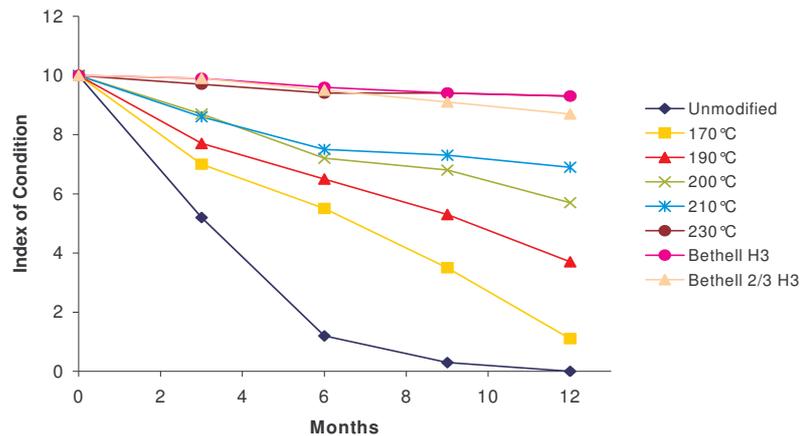


Figure 3: Fungus cellar stakelet tests over 12 months

Mechanical properties

Thermal modification alters the mechanical properties of the wood (Table 1). The reduction in stiffness and strength can be offset by allowances design, or by modifying stiffer timber than would normally be required.

Table 1: Effect on mechanical properties of thermally modified radiata pine as compared to matched samples of kiln dried, unmodified radiata pine

Modification temperature	Stiffness (3.6m length)	Strength (small clear)	Toughness (small clear)
170°C	10% loss	No significant change	No significant change
230°C	20% loss	29% loss	25% loss

Specific end uses

Decking and Cladding

Thermal modification greatly reduces the resin content of radiata pine. This can prevent the formation of sticky resin patches around knots and heartwood. The enhanced dimensional stability of thermally modified wood reduces surface checking and may improve paint adhesion over time (Finnish Thermowood Assn. 2003). The natural decay resistance of thermally modified timber may reduce or eliminate the need for chemical preservatives in exterior applications.

Joinery, Interior and Exterior Furniture

The colour of the modified timber can be controlled by the treatment temperature used, and manipulated as an aesthetic feature. The improved dimensional stability of thermally modified radiata pine is beneficial for furniture and joinery manufacture. Dimensional instability can cause surface checking, loosen joints over time, and cause doors and windows to stick. For exterior furniture, and joinery in damp areas, the decay resistance of thermally modified timber would be an advantage.

Framing

Resistance to decay would be an advantage for timber framing that may be exposed to moisture. This has recently been a problem for some newer houses in New Zealand, and there is a move towards using treated timber for house framing. Improved dimensional stability would decrease movement in the framing over time, reducing problems such as sticking doors and windows, and cracks in wall linings.

CONCLUSIONS

Radiata pine can be thermally modified from green in one simple, fast step. The resulting timber is dimensionally stable, and resists fungal decay. These improved properties would be an advantage for a wide range of end uses. There is some reduction in strength and stiffness of the timber, however this can be overcome by thermally modifying higher grade timber or designing structures to accommodate the reduced properties.

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STUDIES ON THE RELAXATION OF HEAT-TREATED WOOD

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Keywords: Kinetics, rheology, spruce, thermal modification, viscoelasticity

ABSTRACT

Oven-dried sapwood blocks of Norway spruce were heat-treated at four temperatures for five time periods, under nitrogen flow. Oven-dry weight losses (*WL*) due to the treatment ranged from 0.99 to 31.47 %. Following thermal modification, the blocks were conditioned to 65 % RH at 20°C. The short-term steady state relaxation was subsequently examined in pure compression perpendicular to the grain in the tangential direction. Comparisons within the same treatment temperature, showed that heat-treated samples were generally characterised by a lower modulus of relaxation (*MOR_e*). Upon release of the load, modified samples showed a smaller delayed elastic recovery and plastic deformation than untreated wood. Using the kinetic theory of absolute reaction rates to describe the time-dependant behaviour of wood, a single energy barrier was found to dominate the relaxation process. Values of activation energy and activation volume were found to increase with increasing sample *WL*.

INTRODUCTION

Heating wood at temperatures between 110 to 265° C, producing weight losses of less than 20 % reduces the hygroscopicity of the resultant material, improves its dimensional stability and without using fungitoxic chemicals enhances its decay resistance (Gonzalez-Peña *et al.* 2004). Whilst the perceived benefits of the thermal modification of wood might be appealing, it is also clear that heat-treated wood must also be capable of achieving a certain mechanical performance. The behaviour of wood under mechanical stress is time-dependant, relaxation being the decrease of a force necessary to maintain a given state of deformation. The consequence of this behaviour within the first second of stress application is relevant, for instance, for the resonance of musical instruments or during the process of cutting wood. Over a period of minutes to hours, the behaviour has relevance for some operations, such as pressing, drying or bending. The behaviour over extended periods of time, determines the creep of timber members in construction. Despite its practical importance, no information is available regarding the effect of the thermal modification on wood rheology. Indirect results in earlier research suggest that the *MOR_e* might be decreased by such treatment. Contingent evidence also points to the development of deleterious tertiary creep in heat treated wood arising at lower levels of stress than in untreated wood. This study aims to characterise the short term relaxation of heat-treated Norway spruce wood.

EXPERIMENTAL

Oven-dried sapwood samples were thermally treated at 190, 210, 225 and 240°C for five time periods (20, 60, 240, 480 and 960 minutes)

under a slow nitrogen flow, at atmospheric pressure. Following thermal treatment, the short-term steady state relaxation of wood blocks (20 x 10 x 35 mm; R x T x L) was examined; the blocks were stressed in pure compression perpendicular to the grain in the tangential direction. The strain level used was 50 % of the average deformation produced at the proportional limit as previously determined using control specimens. Six replicates were used for each treatment. The complete required deformation was applied in 0.4 seconds, using a universal testing machine (Instron 1195), after which the position of the crosshead was fixed. The stress required to produce the initial strain, and the reducing stress required to maintain this constant strain was measured every second for 180 seconds. *MORel* was calculated as the ratio of the compression stress (varying), over the constant compression strain. All the tests were performed in a room with a controlled atmosphere (65 % RH, 20 ± 2° C), the samples having already equilibrated to these conditions for at least 6 months. After the release of the load, each sample was measured (to ±1 µm) at 8, 480, 8600 and 60,000 s, to determine the plastic deformation and the delayed elastic recovery of the samples. In an attempt to understand the relaxation phenomena at the molecular level and, from there, to develop a model that more accurately predicts the rheological behaviour of wood, a chemical kinetic approach was used to analyse the data (Hanley and Krausz 1974).

RESULTS AND DISCUSSION

For comparison between treatments, the *MORel* is expressed as fractional *MORel* (*fMORel*). Figure 1 shows the *fMORel* vs. ln (time) curves for selected treatments. Generally, it was somewhat difficult to compare the results from different treatments, due to the short testing relaxation period, and dissimilar EMC of the samples. Averaging curves was found to be misleading, so typical curves, the ones numerically most similar to the average curves, were selected for the analysis in each treatment.

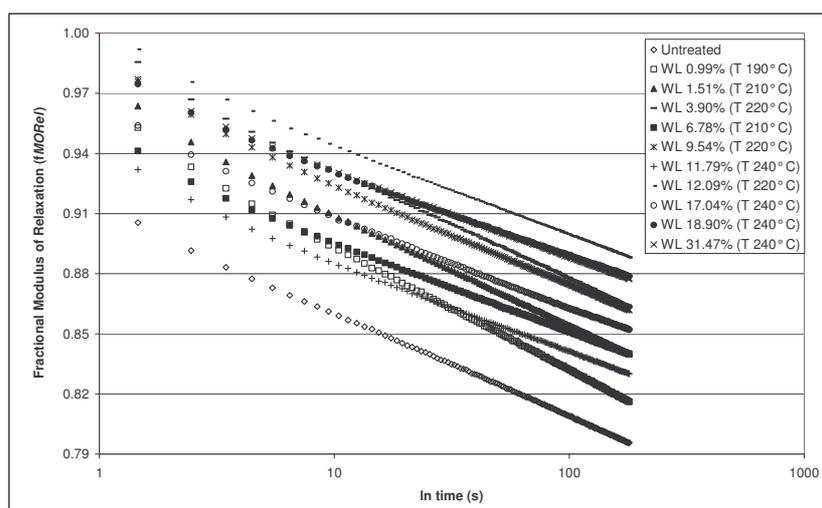


Figure 1: Typical curves on the effect of weight loss due to treatment on Modulus of Relaxation

Figure 1 clearly illustrates the decreasing changing rate in *fMORel* as the *WL* due to the modification increased. Noticeable changes in *fMORel* were more easily resolved for samples with a *WL* > 3%. When

comparisons were made within the same treatment temperature, heat-treated samples were characterised, in most cases, by a direct relationship between $fMOREl$ after 180 s and WL (Table 1). The largest effects in $fMOREl$ were for the samples treated at 225 and 240°C for 16 h. No ultimate effect of the WL on $MOREl$ could be determined when samples from all temperatures were compared together; the trend being that the $MOREl$ was reduced as the WL increased, though. Small differences in the mechanisms of the chemical conversion at different reaction temperatures are proposed to be a major cause for this. It is proposed that the reduction in $MOREl$ could be ascribed to the well established chemical and molecular changes to the wood polymers, e.g. the crystallisation of amorphous cellulose, the breakdown of plastic hemicelluloses, and to the proportionally higher, more condensed lignin content in the modified wood.

Table 1: Thermal treatments and resulting activation volumes and energies upon relaxation

Treat. temp.[°C] time[min]	WL [%]	Moisture content [%]	Initial stress [MPa]	fMOREl [after 180 s]	V _n [m ³ x 10 ⁻²⁶]	ΔE [kJ x mol ⁻¹]	Initial strain [m/m]	Deformation [% Init. strain]	
								d.elast	plastic
Untreated	-	11.54	2.63	.7958	64.83	144.5	.0229	14.3	14.2
190° C									
20'	0.99	10.44	2.36	.8162	65.83	139.0	.0251	11.9	11.0
60'	1.60	9.83	3.95	.8434	48.51	159.8	.0276	12.7	16.6
240'	1.84	9.07	3.51	.8303	55.42	160.0	.0233	18.4	15.6
480'	2.91	8.91	2.92	.8129	65.84	157.4	.0212	11.3	14.4
960'	3.83	8.24	4.48	.8422	43.18	160.2	.0255	12.0	12.3
210° C									
20'	1.51	8.93	3.72	.8401	46.36	149.2	.0242	9.6	14.1
60'	2.90	8.25	3.41	.8188	58.12	156.4	.0239	11.1	12.0
240'	6.06	7.16	4.04	.8208	47.44	157.1	.0270	9.1	9.9
480'	6.78	7.09	3.15	.8398	63.88	165.2	.0258	12.3	11.3
960'	10.94	6.15	2.87	.8300	78.37	176.7	.0227	10.2	8.8
220° C									
20'	3.90	7.48	2.19	.8635	76.49	150.5	.0221	20.7	9.3
60'	7.04	6.78	2.11	.8234	84.64	152.2	.0266	12.6	11.1
240'	9.54	6.24	2.64	.8618	72.30	162.6	.0243	11.2	9.8
480'	12.09	5.70	2.92	.8880	71.50	175.7	.0285	5.1	13.4
960'	18.08	5.69	2.80	.8907	62.13	156.4	.0257	11.0	8.7
240° C									
20'	8.16	6.06	2.78	.8024	62.97	147.1	.0242	9.5	10.5
60'	11.79	5.44	2.61	.8301	79.51	167.8	.0241	7.7	11.4
240'	17.04	5.34	2.42	.8522	88.31	173.9	.0228	9.0	13.2
480'	18.90	5.41	2.56	.8787	89.91	187.0	.0251	7.5	8.4
960'	31.47	5.74	1.84	.8778	117.60	179.7	.0207	8.0	10.9

After releasing the load, heat-treated samples showed in general, a smaller delayed elastic recovery and plastic deformation as the WL increased (Table 1). These were calculated as the instantaneous (at 8 s) minus the long term (at 60,000 s) strain recovery and as the long term strain recovery (at 60,000 s), respectively. As the treatment causes chemical changes and lining up of the hemicelluloses along the microfibrils, and cellulose microfibrils to increase their crystallinity, it is proposed that the smaller delayed elastic and plastic deformation of modified wood is because these changes prevent wood polymers from uncoiling and/or slippage under stress. Polymer bonds are successively broken and re-established during plastic flow, so the process is identical with a chemical reaction, and the movement of dislocations in the wood microfibrils, fully corresponds to the isomerisation of a giant molecule. Using the kinetic theory of absolute reaction rates to describe wood relaxation, it was determined that a linear regression was a good fit to the data of the natural logarithm of the rate of stress relaxation [$\ln(-\dot{R})$] as a function of stress level (τ) (Figure 2). Therefore, a single energy barrier was proposed to dominate the relaxation process in all cases. Values of activation energy (ΔE) and activation volume (V_{fi}) were

found to increase with increasing sample WL (Table 1). As wood is being stressed in compression, external work is done on the specimen. However, the process of compressing wood is *quasi-adiabatic*, and thus most of the energy is used to increase the internal molecular energy in the wood substance. Since the energy used to dissociate hydrogen bonds increases in line with polymer crystallinity, a plausible explanation for an increase in ΔE at larger WL , may lay in the molecular changes undergone mainly on cellulose, largely in the form of lateral crystallite growth, which results in an increase of the overall energy values required for the polymers to participate in the flow process and stress relaxation. Similarly, larger V_{fi} are required in modified samples to produce the equivalent amount of polymer flow.

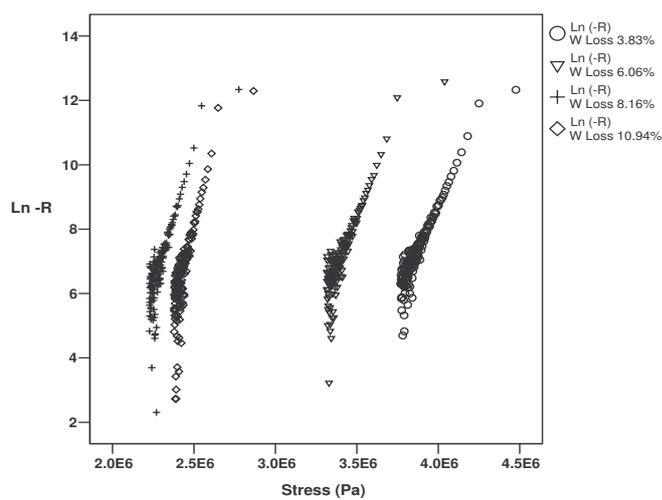


Figure 2: Stress relaxation rate dependence on stress (selected samples of heat-treated wood)

CONCLUSIONS

In this work, the effect of weight loss on the short-term stress relaxation in small blocks of heat-treated spruce wood was investigated. Modified samples were characterised, in general, by a reducing $MOReI$ as the WL due to the modification increased. It is proposed that the lower $MOReI$ of heat-treated wood, coupled with its established reduced mechanical strength, could lead to earlier wood failure in zones of localised stresses, or to split readily upon rapid changes in wood moisture content in service. Prospective benefits of a lower $MOReI$ are a better performance during pressing for gluing of laminates, or the production of particleboards due to the smaller 'springback' observed in modified wood.

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TECHNOLOGICAL IMPROVEMENT OF PORTUGUESE EUCALYPT AND PINE WOODS BY HEAT TREATMENT

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Keywords: Dimensional stability, Equilibrium moisture content, *Eucalyptus globulus*, Heat treatment, Mechanical resistance, *Pinus pinaster*.

ABSTRACT

Heat treatments for the technological improvement of wood were made in the presence of air using two important species grown in Portugal: the hardwood *Eucalyptus globulus* and the softwood *Pinus pinaster*. The heat treatment was made using an oven during 2 to 24 h and temperatures of 170°C, to 200°C. Mass losses increased with treatment time and temperature. Anti Shrinking Efficiency (ASE) between treated and untreated samples was calculated at 35 %, 65 % and 85 % relative humidity for radial and tangential directions. Bending strength and modulus of elasticity (MOE) were also determined. Equilibrium moisture content (EMC) of heat-treated wood decreased for pine and eucalypt wood by 57 % and 67 %, respectively. Radial ASE_{35%} for eucalypt wood was higher than for pine wood, reaching respectively 87 % and 73 %. Tangential ASE_{35%} was usually higher than radial. ASE_{65%} and ASE_{85%} showed behaviour similar to ASE_{35%} but was smaller. All ASE values increased with temperature and treatment time. Bending strength and MOE decreased with mass loss.

INTRODUCTION

The use of thermal treatments to modify properties of wood is not new. Some early studies to improve wood dimensional stability were carried out by Stamm *et al.* (1946). More recently, environmental concerns have stimulated the search for methods to preserve wood without the use of chemicals, and heat treatment processes have evolved all over Europe, namely Thermowood in Finland, Plato Wood in Holland, Retification and Bois-Perdure in France and Menzholz in Germany.

Pinus pinaster and *Eucalyptus globulus* are two of the forest species with the greatest planted area in Portugal. Pine wood is used for all kinds of furniture, although for outdoor use it must be treated, since it is considered a low durable species by NP EN 350-2. Until last year, it was mainly treated with CCA and currently with CCB. *Eucalyptus globulus* is used almost exclusively for pulp production. Old eucalypts with very high extractives content are not adequate for pulp and are used as firewood or for some less demanding pieces of furniture. Eucalypt wood is considered to be non durable by NP EN 350-2, with high dimensional instability and very difficult to treat, even with the use of pressure, since it is almost impossible to impregnate. The impregnation is only possible for small diameter wood without heartwood and there is a considerable leaching of preservative solution because of the large diameter of vessels in the wood. Even treated eucalypt wood is susceptible to soft-rot fungus attack (Reimão and Nunes 1989). Heat treatment can improve dimensional stability and rot

resistance so that wood can be used outdoors without chemicals and compete with tropical wood of higher cost.

EXPERIMENTAL

Pine (*Pinus pinaster* Aiton.) and eucalypt (*Eucalyptus globulus* L.) wood came from the Portuguese region of Águeda. Samples for heat treatment were cubic with around 40 mm edge size with clear radial, tangential and transversal faces. Samples were kept in a conditioned room with 50 % humidity and 20°C for three weeks. Equilibrium moisture and mass of all the samples were determined. Oven heat treatment was made in the presence of air during 2, 4, 6, 8, 12 and 24 h at 170°C, 180°C, 190°C and 200°C. After treatment, the samples were cooled in a dry environment and weighted. Mass loss was determined in relation to dry wood. The treated and untreated samples were kept in an oven at 20°C and 35 % relative humidity. After stabilisation, the samples were weighed and measured in radial, tangential and transverse directions. The same procedure was done using 65 % and 85 % relative humidity. Dimensional stability was determined by the ASE (Anti Shrinking Efficiency) method used by Stamm (1946), which gives the shrinking difference between treated and untreated samples. ASE 35%, ASE 65% and ASE 85% correspond to shrinking differences between the corresponding relative moisture and the dry state, determined in radial or tangential directions. Total ASE corresponds to volume difference at 35 %, 65 % and 85 % relative humidity (RH). MOE and bending strength of treated and untreated wood were measured using a three point bending device. Measurements were made using a constant velocity of 0.3 mm/min for MOE. The velocity for bending strength was estimated as the velocity so that the sample breaks after 3 min.

RESULTS AND DISCUSSION

Mass loss

Mass loss of heat treated pine wood was in general smaller than heat treated eucalypt wood at the same temperature and time of treatment. However, the difference was very small. As an example, mass loss was 2.2 % for pine wood and 2.7 % for eucalypt wood treated during 4 h at 190°C.

Equilibrium moisture content

EMC decreased for all treated samples, even at 170°C and during only two hours. EMC decreased with heat treatment especially for 35 % RH. At the same temperature and time of treatment, the decrease was higher for eucalypt wood. EMC of pine wood at 35 % RH, treated for 24 h, decreased 46 %, 53 %, 57 % and 56 % of initial EMC, for 170°C, 180°C, 190°C and 200°C. For 65 % and 85 % RH, the decrease was smaller, e.g. the maximum decrease was 48 % and 46 % respectively. For eucalypt wood treated for 24 h, the EMC at 35 % RH decreased 61 %, 69 %, 67 % and 67 % of initial EMC, for 170°C, 180°C, 190°C and 200°C, while for 65 % and 85 % RH, the EMC decreased only 59 % and 48 %, respectively (Figure 1).

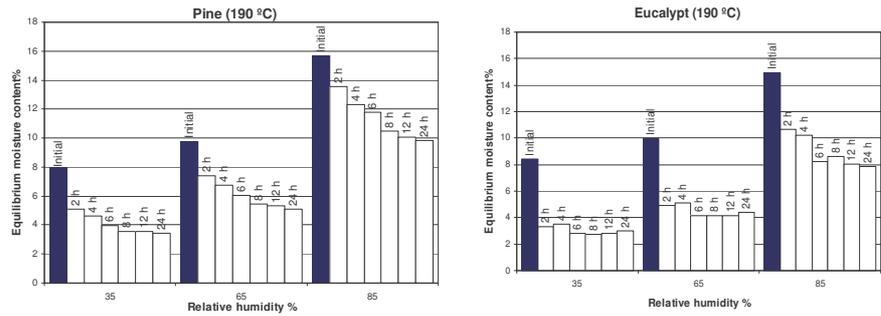


Figure 1: Equilibrium moisture content for heat treated pine and eucalypt wood for 35 %, 65 % and 85 % relative humidity (Example for 190 °C)

Dimensional stability

Radial ASE_{35%} increased with time and temperature of treatment. Maximum ASE_{35%} values were 65 %, 63 %, 64 % and 73 % for pine wood and 76 %, 85 %, 89 % and 88 % for eucalypt wood at 170°C, 180°C, 190°C and 200°C, respectively. Radial ASE_{65%} and ASE_{85%} also increased with time and temperature of treatment but with smaller values. Maximum values for Radial ASE_{65%} were 37 %, 52 %, 61 %, 55 % for pine wood, and 59 %, 73 %, 69 %, 71 % for eucalypt wood and for ASE_{85%} they were 31 %, 40 %, 36 %, 39 % for pine wood and 39 %, 45 %, 53 % 50 % for eucalypt wood at 170°C, 180°C, 190°C and 200°C, respectively. Tangential ASE showed an identical behaviour, with higher values than radial ASE (Table 1). Total ASE had intermediate values between radial and tangential ASE, since there was almost no difference in axial length. Although untreated eucalypt samples had higher swelling than pine, treated samples showed smaller swelling.

Table 1: ASE for heat treated pine and eucalypt wood at 190 °C conditioned at 35% relative humidity

Temp. [°C]	Time [h]	ASE _{35%} [%]					
		Pine			Eucalypt		
		Radial	Tangential	Total	Radial	Tangential	Total
190	2	56.7	61.5	60.0	77.0	72.6	74.4
	4	45.9	67.6	59.5	83.6	83.3	83.6
	6	63.7	73.2	70.0	78.5	85.7	83.2
	8	63.6	73.3	69.1	81.6	90.6	87.5
	12	63.5	74.3	70.7	81.1	87.6	85.4
	24	64.4	74.7	70.0	88.7	95.7	93.2

Radial, tangential and total ASE at 35 %, 65 % and 85 % RH increased with mass loss, the increase being higher for smaller mass losses. Results were better for eucalypt wood than for pine wood treated at the same time and temperature. When comparing results, at the same mass loss, eucalypt ASE values were better than pine's. For example with 3 % mass loss Radial ASE_{65%} was 80 % for eucalypt and 52 % for pine wood.

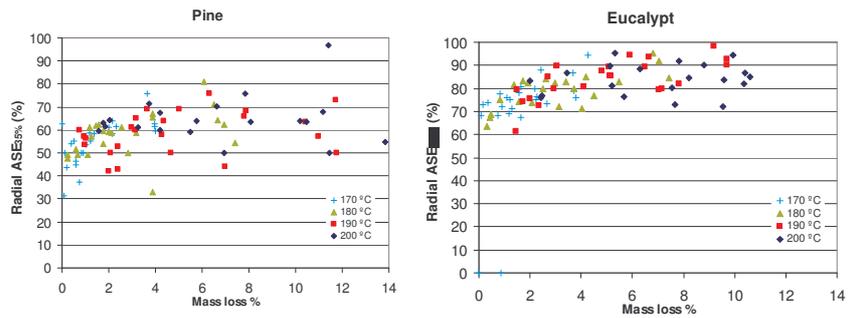


Figure 2: Variation of Radial ASE_{35%} with mass loss for heat-treated pine and eucalypt wood.

Mechanical resistance

MOE of heat-treated pine wood decreased with mass loss. The decrease was under 5 % for mass losses until 4 %, reaching 20 % for a 12 % mass loss. MOE of heat-treated eucalypt wood showed a similar behaviour, although some values contradicted this tendency, *i.e.* it seemed to decrease less until 7 %, decreasing more after this point and reaching 25 % at 10 % mass loss. Bending strength of heat-treated eucalypt and pine wood showed a high variability. Despite this, bending strength of heat-treated pine wood seemed to decrease about 30 % for 4 % mass loss reaching 60 % for mass losses higher than 6 %. Bending strength of heat-treated eucalypt wood decreased about 30 % for 4 % mass loss and about 60 % for 10 % mass loss.

CONCLUSIONS

Heat treatment decreased the equilibrium moisture content of wood and increased its dimensional stability but decreased MOE and bending strength. Stability improvements were better for the tangential direction and for low relative humidity. Improvements were better for eucalypt wood than for pine wood. Heat treatment seems to be a viable process for eucalypt wood now used almost exclusively for the production of pulp for paper.

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ANATOMICAL AND MECHANICAL PROPERTIES OF *POPULUS TREMULOIDES* AND *PINUS BANKSIANA* DURING THE DIFFERENT STAGES OF TIMBER-TRANSFORMATION UP TO HEAT-TREATMENT

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Keywords: *Populus tremuloides*, *Pinus banksiana*, wood anatomy, radial hardness, modulus of rupture, modulus elasticity

ABSTRACT

Heat treatment is a wood transformation technology newly introduced in North-America. *Populus tremuloides* cellular changes during different transformation stages (logging, sawing, drying with maximum heat values of 80°C and 220°C) were examined. These examinations were conducted on thin slides observed under microscope. *Pinus banksiana* was analysed for cellular state, radial hardness, modulus of rupture (MOR) and modulus of elasticity (MOE) at final drying temperature of 120, 160, 190 and 220°C. We observed an increasing number of cellular defects in *Populus tremuloides* during the lumber conversion stages. Similar observations were noted in *Pinus banksiana* with the increasing final drying temperature. The values of MOR decreased significantly between 160°C and 190°C in *Pinus banksiana* whereas the values of MOE and radial hardness slightly varied within the final drying temperatures without a clear tendency.

INTRODUCTION

Populus tremuloides Michx. and *Pinus banksiana* Lamb. are common tree species in the boreal forest of Quebec, Canada. Both species are commercially used, but the economical value of the lumber is low. In order to increase the economical value of these two species, different heat treatments have been conducted in the last few years. These processes, tested between 200°C and 240°C, were used to induce chemical modifications of the wood, which results in new wood properties. Heat treatment has a direct effect on the three wood polymers, cellulose, hemicellulose and lignin. Those changes can influence the cellular state and the mechanical properties of the wood. In Europe, the main tree species were already tested with a similar process and relationships were established between the drying temperature and the cellular state as well as the mechanical observation. There is currently a lack of information for the tree species in North America.

The evaluation of the wood properties of these two species was realised by analyzing first, the timber transformation at different states and second at different temperatures up to the heat-treatment. At each given period of timber transformation, samples were taken to evaluate the cellular conditions and some mechanical properties. In the case of *Populus tremuloides*, the cellular state was analysed after tree logging, sawing and drying treatments of 80°C and 220°C respectively (the maximal heat in both cases). In the case of *Pinus banksiana*, the cellular state, the radial hardness, the modulus of rupture (MOR) and the

modulus of elasticity (MOE) were measured at final drying temperature of 120, 160, 190 and 220 °C.

EXPERIMENTAL

Material

Populus tremuloides – nine trees were selected and samples taken after each step of transformation: logging, sawing, drying at 80°C and drying at 220°C.

Pinus banksiana – nine boards were analysed for each final temperature of heat-treatment: 120°C, 160°C, 190°C and 220°C. A thermocouple was placed inside each board to measure the temperature evolution and the final temperature of each wood.

Cellular state

For each sample step and each drying temperature, a small wood piece was used to evaluate the cellular state of the wood. Fine transversal slides were cut by means of a microtome and pictures taken with a Polaroid (3.2 megapixels) and at a magnification of 200X under a microscope. The cell numbers on each photo was counted as well as cell wall collapses and cracks to quantify the deterioration.

Mechanical tests

Hardness

One sample for each temperature was used to determine the radial hardness following the US standard ASTM D1324-83 and with a dimension of 35 mm x 35 mm x 200 mm.

Three points static bending

Following the US standard ASTM D-143, MOE and MOR were measured for three samples on each board for each analysed final temperature. The sample dimension was 13 mm X 13 mm X 192 mm.

Statistical analysis

For each properties of interest, an analysis of variance with one factor (Oneway Anova) was conducted. Significant means were compared using a Tukey test.

RESULTS AND DISCUSSION

Populus tremuloides

Cell wall collapses were observed in each transformation step, after logging, sawing, drying at 80°C and 220°C respectively (table 1). The number of cell wall collapses increased from logging to drying at 80°C, but no significant differences were noted between the drying process at 80°C and 220°C. The number of cracks is nearly absent after logging, increased lightly after sawing and drying at 80°C (table 1). An important increase in the number of cracks was detected by exposing the wood to a drying heat of 220°C. These results showed a negative influence of the different timber transformation steps on the cell wall quality.

Pinus banksiana

Cell wall collapses and cracks were combined and a significant increase of these two defects was measured between drying at 120°C and drying at 220°C (Table 1).

For MOE, no significant differences were noted between the mean measurements at 120° and 220°C, whereas a significant difference was calculated between the final drying temperature at 160° and 190°C. A significant decrease of MOR was measured between drying temperature 160° and 190°C. The difference between the drying temperature of 120° and 160°C, as well as between 190°C and 220°C was not significant. The radial hardness showed no differences between the four final drying temperatures (table 2). These results reveal that cell wall component seem to react to high drying temperatures. Depolymerization might occurs, creating cell defects and influenced negatively the MOR.

Table 1: Mean percentage of cellular defects at different lumber transformation steps and at drying temperatures for both species

Species	Type of deterioration	Logging (%)	Sawing (%)	Drying 80°C (%)	Drying 120°C (%)	Drying 220°C (%)
<i>Populus tremuloides</i>	Cell wall collapss	3.7	6.3	5.0		5.1
	Cracks	3.4	9.8	17.1		34.3
<i>Pinus banksiana</i>	Cell defects				52.7	69.3

Table 2: Mean values of MOE, MOR and radial hardness of *Pinus banksiana* at four different drying temperatures

Mechanical properties	Drying temperature (°C)			
	120	160	190	220
MOE (N/mm ²)	7711 _{a,b}	8775 _a	6841 _b	8110 _{a,b}
MOR (N/mm ²)	86 _a	81 _a	62 _b	59 _b
Side Hardness (Hm)	14 _a	15 _a	15 _a	13 _a

** Levels not connected by same letter are significantly different

CONCLUSION

The cellular quality of *Populus tremuloides* decreased with each step of timber transformation with a small number of cracks and cell wall collapses after logging but this number increased after sawing and drying at 80° and 220°C. To improve the final product, each timber transformation step should be taken into consideration. A significant increase of cell deterioration was also observed between drying at 120° and 220°C in *Pinus banksiana*. The MOR values decreased significantly between the final drying temperature of 160° and 190°C. The results were more variable for the radial hardness and MOE between the drying temperatures. Thermal treatment seems to affect wood cell wall polymer, especially between 160°C and 190°C and wood treated over 190°C may not be suitable for structural use.

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CHAPTER 2

ACETYLATION

THE DECAY RESISTANCE OF ANHYDRIDE MODIFIED WOOD: A STUDY OF THE MECHANISMS

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Keywords: Anhydride, cell wall, *Coniophora puteana*, decay resistance

ABSTRACT

This paper reports on part of an ongoing comprehensive investigation into the decay resistance of anhydride modified wood. Corsican pine, beech and rubberwood were modified with acetic and hexanoic anhydride and the modified wood exposed to *Coniophora puteana*. It was confirmed that with Corsican pine, the decay resistance was determined by the weight percentage gain (WPG) due to modification only, rather than extent of hydroxyl substitution. This indicates that the decay resistance is due to a physical blocking phenomenon, such as a reduction in cell wall moisture content and/or blocking of the cell wall micropores. With anhydride modified rubberwood, the decay resistance was determined by the extent of OH substitution, indicating that the protection mechanism was related to a blocking of a substrate recognition process. Modified beech exhibited more complex behaviour. In addition, the FSP of samples of modified Corsican pine was determined using solute exclusion and it was found that this data correlated with the extent of cell wall bulking due to modification as determined by helium pycnometry. Finally, preliminary results of the relationship between time of fungal exposure and decay resistance are presented.

INTRODUCTION

Although the decay resistance of anhydride modified wood has been the subject of many investigations, there is still much uncertainty as to the exact mechanisms by which microbial decay resistance is imparted to the wood. Since the anhydride modification process results in the substitution of cell wall hydroxyl (OH) groups with acyl moieties, the possibility that decay resistance is related to the inability of cell wall degrading enzymes (cellulases, hemicellulases, ligninases) to recognise the substrate has been proposed. However, it is now well established that such enzymes are not able to enter the cell wall of undegraded wood. Thus, except in circumstances where cell wall degradation proceeds from the surface inwards, substrate blocking of enzyme activity (a biochemical mechanism) cannot be responsible. Due to the lack of access of the undegraded cell wall interior to enzymes, low molecular weight degradative agents (LMWDA's) have been proposed, which are capable of chemically attacking the cell wall macromolecular components, thereby increasing the size of the cell wall micropores resulting in improved accessibility for the enzymes. It is therefore possible that substitution of cell wall OH groups is responsible for blocking attack by LMWDA's (a chemical mechanism).

The bonded acyl groups within the cell wall occupy space, which is thereby denied to water molecules; as a result of this, the fibre saturation point (FSP) of the modified wood is reduced. Fungi require a minimum moisture content (MC) in order to decay wood, and it is possible that a reduction of cell wall MC due to modification imparts decay resistance. Finally, the presence of acyl groups serves to take up space within the cell wall micropores, which might prevent the ingress of degradative agents. These latter two mechanisms can be considered to be physical processes.

By modifying wood with anhydride reagents of different molecular weight, it is possible to determine whether substitution of OH groups or a physical bulking (blocking) process is responsible for imparting decay resistance.

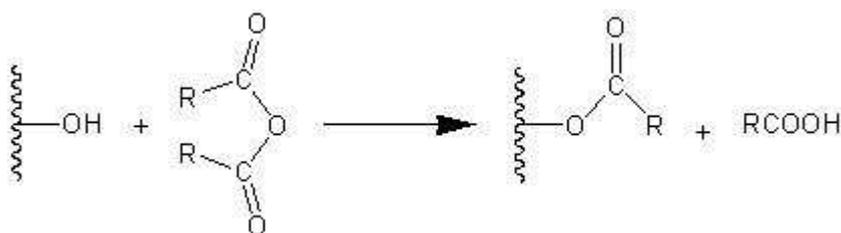


Figure 1: Schematic of the wood anhydride reaction

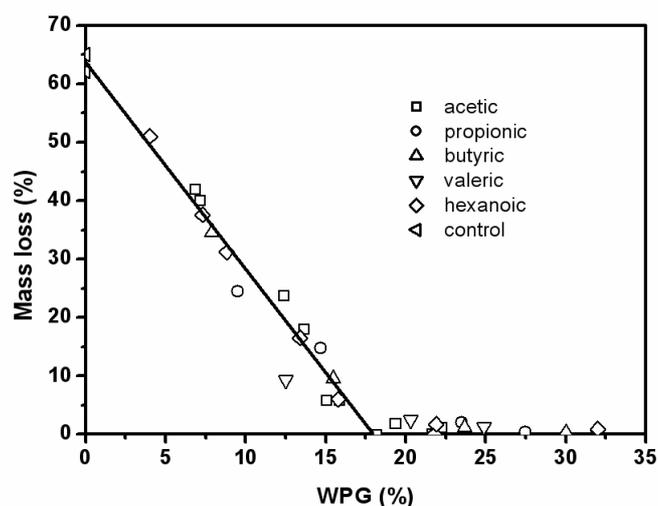


Figure 2: Relationship between decay resistance and WPG for modified Corsican pine exposed to *Coniophora puteana*

As part of a comprehensive study of the physical and biological properties of anhydride modified wood, several studies were undertaken to determine the relative importance of OH substitution and cell wall bulking in imparting decay resistance. This has involved the reaction of Corsican pine with a range of anhydride reagents (Figure 1: acetic R=CH₃, propionic R=C₂H₅, butyric R=C₃H₇, valeric R=C₄H₉, hexanoic R=C₅H₁₁) and determining the decay resistance against the brown rot fungus *Coniophora puteana*. Results from this study have been presented previously (Papadopoulos and Hill 2002, Hill *et al.* 2003), and are reproduced in Figure 2.

This shows clearly, that it is only cell wall bulking that is responsible for imparting decay resistance (since this is proportional to WPG). This work has now been extended to determine whether cell wall micropore blocking or a reduction in cell wall MC is the mechanism responsible. Furthermore, it was also of interest to determine whether cell wall bulking is a generic decay protection mechanism, so the study was extended to other wood species, as well as repeating the work with Corsican pine. Finally, since, up until now, these studies have been performed using a 16 week exposure period, it was decided to investigate the progress of decay in modified wood, by using different exposure periods. The results from all these studies are reported herein.

In order to determine the relationship between cell wall MC and decay resistance, it was necessary to develop a method for the determination of FSP at different WPG's. The method chosen for this was solute exclusion, which involves the immersion of a wood sample in a solution of a sugar of known diameter. After allowing for equilibrium to be established, the concentration of the solute in the probe solution is determined using differential refractometry. Depending upon the size of the sugar molecule (the probe), it will have a certain accessibility to the cell wall of the wood. If solutions of progressively larger probes are used, then a point is reached when the cell wall is no longer accessible. By using this method, it is possible to determine the fibre saturation point of the wood.

In order to examine the relationship between FSP and bulking of the cell wall of the wood by modification, the technique of helium pycnometry was applied. This uses helium as the displacement medium in order to obtain highly accurate values for the volume occupied by the wood material. Cell wall volume change was determined by using helium pycnometry of identical wood samples prior to and after modification.

EXPERIMENTAL

All experimental methods have been reported in detail in various publications (Papadopoulos and Hill 2002, Hill *et al.* 2003, Hill and Ormondroyd 2004, Hill *et al.* 2005). For the present studies, the relationship between cell wall MC and decay resistance was investigated for acetic anhydride modified Corsican pine only. Three wood species were selected for the investigation of the mechanism(s) of decay resistance Corsican pine (*Pinus nigra*), beech (*Fagus sylvatica*), and rubberwood (*Hevea brasiliensis*). For the study of the change in decay resistance in relation to time of exposure to fungal attack, Corsican pine was modified with acetic or hexanoic anhydride. The fungus selected for these studies was the brown rot fungus *C. puteana* (FPRL 11E).

RESULTS AND DISCUSSION

Molar volume determined using helium pycnometry

The relationship between molar volume and WPG for acetic anhydride modified wood at a variety of WPG's is shown in Figure 3.

This plot shows that there is a constant relationship between the volume occupied per mole of acetyl groups and WPG. One of the data

points (at 4 % WPG) appears anomalously high in this analysis and was not employed for data fitting purposes. This analysis results in a molar volume of 33 cm³ per mole of anhydride being determined (Hill and Ormondroyd 2004).

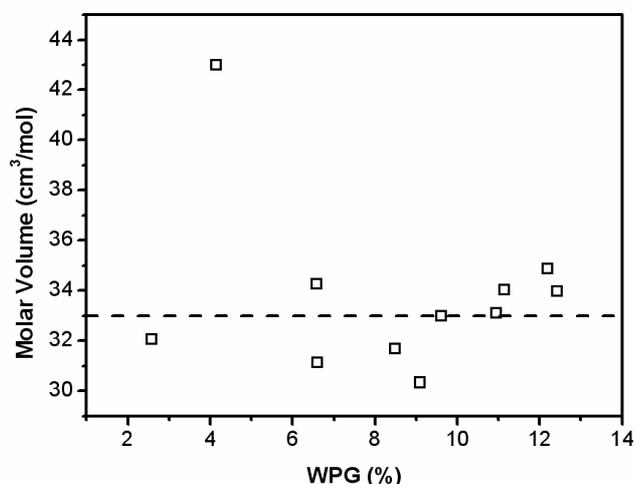


Figure 3: Relationship between molar volume and WPG determined using helium pycnometry

Solute exclusion and FSP

A plot from the solute exclusion experiment for unmodified Corsican pine is shown in Figure 4a, and for Corsican pine acetylated to 20.7 % WPG in Figure 4b.

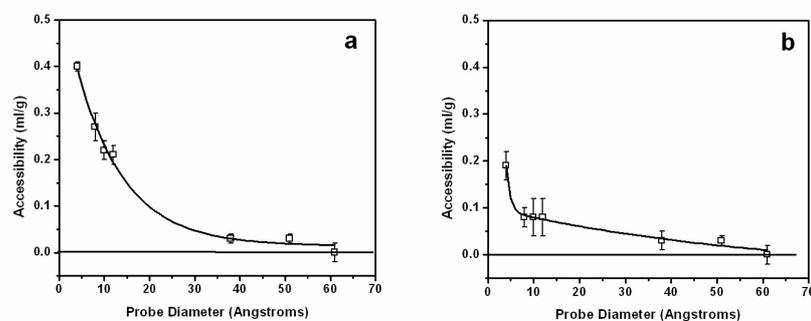


Figure 4: Results for solute exclusion experiment on unmodified Corsican pine and Corsican pine (a) modified to 20.7 % WPG (b) showing accessibility of different diameter probe molecules

From these studies on Corsican pine modified to a variety of WPG's with acetic or hexanoic anhydride, it is possible to determine the relationship between FSP and extent of modification of the wood. This corresponds to the value obtained with the smallest probe (water) subtracted by the value obtained using the largest diameter probe (already done in these plots). When this is done, the relationship between FSP and WPG is as shown in Figure 5 (Hill *et al.* 2005)

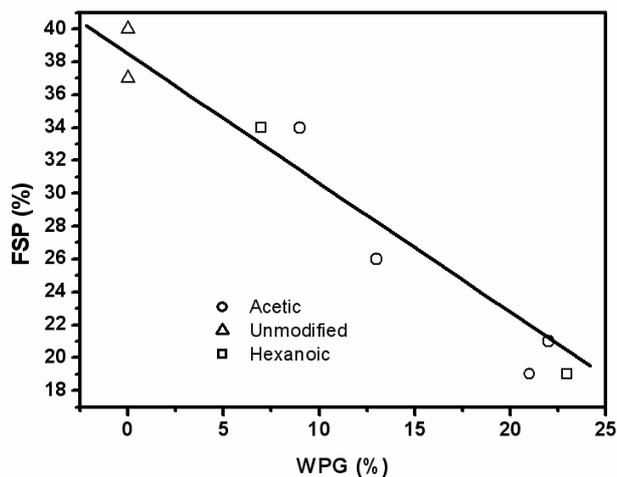


Figure 5: Relationship between FSP (determined using solute exclusion) and WPG with the straight line showing the calculated FSP obtained from helium pycnometry measurements of molar volume

The linear fit to the data was calculated using the helium pycnometry data. This technique gives a very accurate measurement of the volume occupied by the acetyl substituents in the cell wall. By assuming that this volume corresponds to cell wall volume no longer available to water molecules, and assuming the FSP of the unmodified wood to be 38 %, the linear fit was constructed. The excellent fit between the solute exclusion FSP data and the linear relationship calculated from the helium pycnometry data is very strong evidence indicating that the reduction in FSP is due to cell wall bulking by the bonded acyl groups.

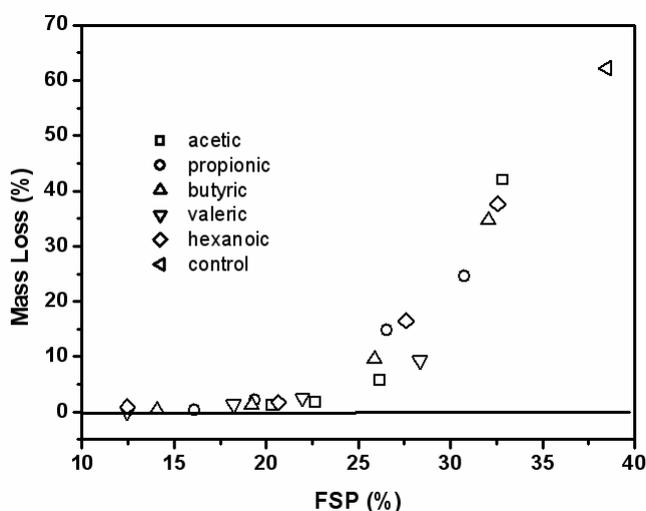


Figure 6: The relationship between FSP and decay mass loss for modified Corsican pine exposed to *C. puteana*

Finally, it is possible to combine the two sets of data to yield the relationship between FSP and decay mass loss, as shown in Figure 6. This indicates that the zero mass loss decay threshold corresponds with a FSP value of the order of 20 %. In a study of the decay of unmodified Scots pine (*Pinus sylvestris*) and Norway spruce (*Picea abies*) by *Coniophora puteana*, it was reported that the moisture content of the wood had to exceed 25% before decay would occur (Viitanen and Paajanen 1988). The close correspondence between the threshold FSP values obtained in this work and those reported previously for unmodified wood are of interest.

Effect of wood species on decay resistance of modified wood

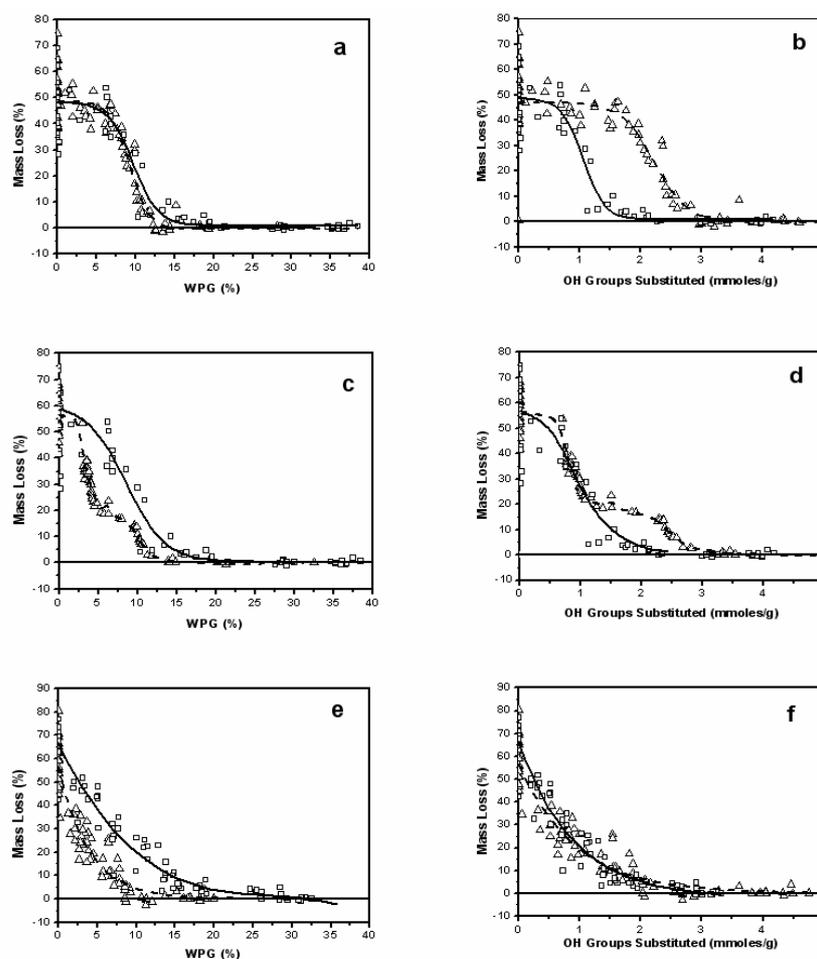


Figure 7: Relationship between decay resistance and WPG for Corsican pine (a), beech (c), and rubberwood (e), and relationship between extent of OH substitution and decay resistance for modified Corsican pine (b), beech (d), and rubberwood (f), acetylated (triangles), hexanoylated (squares)

Figure 7 shows the results from a recent study of the decay resistance of Corsican pine, beech, and rubberwood modified with acetic or hexanoic anhydride to a variety of WPG's. With anhydride modified Corsican pine, it can be seen that the mass loss due to decay is a function of WPG, irrespective of anhydride, in agreement with previous reports. However, this behaviour is not exhibited by modified beech, or rubberwood. In the case of rubberwood, the extent of OH substitution is the factor determining the decay resistance, whereas with beech, this is only true up to a WPG of 5 %. Beech exhibits more complex behaviour, in that up to a WPG of 5 %, there is a significant improvement in decay resistance, but between 5 and 10 % WPG there is little change. Further increases in the level of reaction then result in an increase in decay resistance, until the zero decay threshold of 15 % WPG is obtained. The reason for this behaviour is not known, but may relate to the relative rates of reaction of the OH groups associated with the different macromolecular cell wall components. It is posited that rapid substitution of the more accessible OH groups associated with the hemicelluloses leads to protection of this component at relatively low WPG's, whereas more extended reaction times are required to protect

the cellulose. It is interesting to note that there is no evidence of this behaviour with the hexanoic anhydride modified beech, which may be related to differences in the reaction kinetics between the two anhydrides (Hill 2003).

With rubberwood, the evidence clearly shows that the extent of OH substitution is the factor determining decay resistance, indicating that the protection mechanism involves blocking of a substrate recognition process. The reason why there is such a fundamental difference in the mechanism of decay protection between these species is not known at present. Another point to note is the initial part of the plot of modified Corsican pine up to a WPG of around 7 %, where the linearity of the relationship between ML and WPG is lost. Again, the reason for this behaviour is not known, but again, could possibly be related to rapid reaction of the hemicellulose components by reagent already located in the cell wall due to pre-impregnation of samples prior to reaction. As the extent of reaction increases the influence of WPG (bulking) becomes more significant.

Decay resistance and time of exposure in decay tests

Most reports of the decay resistance of anhydride modified wood are based on various standards and as a consequence report the results after a pre-determined exposure period. The threshold WPG where zero decay mass loss is found is usually reported. What is not known is whether such a threshold represents an absolute WPG limit to prevent decay, or whether the threshold relates to the time that the modified wood is exposed. In order to study the effect of time of exposure to fungus upon the threshold value, a series of experiments are underway using *C. puteana* and different exposure periods. The preliminary results from this study are shown in Figure 8. Although only two time periods have been studied thus far, with the 12 week exposure test performed at BRE and the 16 week test at Bangor. From this preliminary data, it would seem that there is no significant change in the decay protection threshold, although further work is underway to verify this tentative conclusion.

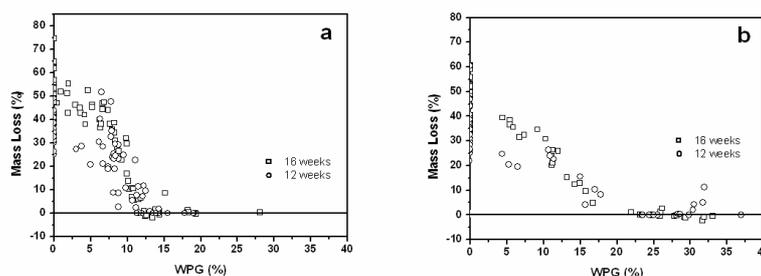


Figure 8: Preliminary results from the time series decay experiment for acetylated (a) and hexanoylated (b) Corsican pine exposed to *C. puteana*

CONCLUSIONS

Modification of wood with different chain length anhydrides allows for an examination of the relative importance of cell wall bulking compared to OH substitution in determining decay resistance. This work has shown that there is a significant difference in the decay protection mechanisms between anhydride modified Corsican pine, beech and rubberwood. With Corsican pine, the decay protection is related to cell wall bulking only, which may either be due to a reduction in cell wall

MC, or to blocking of the cell wall micropores. With rubberwood, decay protection is related to the extent of OH substitution, indicating that a substrate recognition process is being prevented. Beech apparently exhibits more complex behaviour, although further work needs to be performed to ensure that this is not an experimental artefact. Preliminary findings on the effect of time of exposure to fungal attack by *C. puteana* seem to indicate that there is no change in the WPG decay protection threshold.

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THE INFLUENCE OF ACETYLATION OF RADIATA PINE IN STRUCTURAL SIZES ON ITS STRENGTH PROPERTIES

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Keywords: Radiata pine, acetylation, mechanical properties, structural sizes

ABSTRACT

In much of the literature on the properties of wood that is enhanced by acetylation, the strength properties are said to be not affected. In many cases this has been measured with a flexure test, determining strength (MOR) and stiffness (MOE) of small pieces of clear wood. In the calculation of constructions, structural engineers need to work with more realistic values.

In this study Radiata pine of structural sizes was tested in a 4-point flexure test according to EN 408, in order to assess MOR and MOE. Firstly, the MOE was determined non-destructively for untreated timber. Secondly, the same pieces were acetylated to 20 % acetyl content. Thirdly, these pieces were tested in order to determine the MOE and MOR after treatment. The MOR and MOE of untreated Radiata pine were also determined using pieces of the same origin. The density of all test specimens was recorded as well.

According to EN 338 the characteristic strength and stiffness values of (North) European softwood can be determined based on the MOR, MOE and the density. It is not clear if the same relationships can be used for (treated) Radiata pine. The verification of these relations will be the subject of study in the near future using the same material as used for the four point bending tests described in this paper.

INTRODUCTION

The past decades, extensive research has been done on acetylation with uncatalysed acetic anhydride to upgrade the durability and dimensional stability of not-durable wood species (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, Rowell *et al.* 1989, Singh *et al.* 1992).

For load-bearing applications, of which outdoor structures, like timber bridges, are most interesting regarding the durability properties, the mechanical properties of acetylated wood are of major importance. According to the literature the mechanical properties are not significantly altered by acetylation (Akitsu *et al.* 1993, Bongers and Beckers 2003, Dreher *et al.* 1964, Goldstein *et al.* 1961, Larsson and Tillmann 1989). In many cases this has been measured with a bending test, determining strength (MOR) and stiffness (MOE) of small pieces of clear wood. In the calculation of constructions, however, structural engineers need to work with more realistic values, based on the properties of structural sizes.

In this study, Radiata pine of structural sizes was tested in a 4-point bending test according to EN 408, in order to determine these characteristic bending stiffness (MOE) and –strength values (MOR) of untreated as well as acetylated Radiata pine.

EXPERIMENTAL

Radiata pine (*Pinus radiata* D. Don) boards of 50 mm thickness, 155 mm width and 4 m length, visually graded as No 2 Clear and Better (one face and both edges have no visible defects), grown in New Zealand, are used in this study to determine the bending stiffness and –strength according to EN 408.

After conditioning at 65 % relative humidity and 20 °C during 3 weeks, all boards have been visually assessed on wood quality parameters such as distortion, knots, slope of grain, etc. The moisture content and weight of the boards was also measured. Further, the static bending stiffness (Modulus of Elasticity MOE) of 44 boards of Radiata pine was (non-destructively) determined by 4-point flexure test over a span of 2.8 m, which was classified as the “weakest” part of the board by visual assessment. This part is loaded to approximately 40 % of the estimated bending strength to determine the bending stiffness before acetylation. In Figure 1 a schematic overview of the test set-up is given.

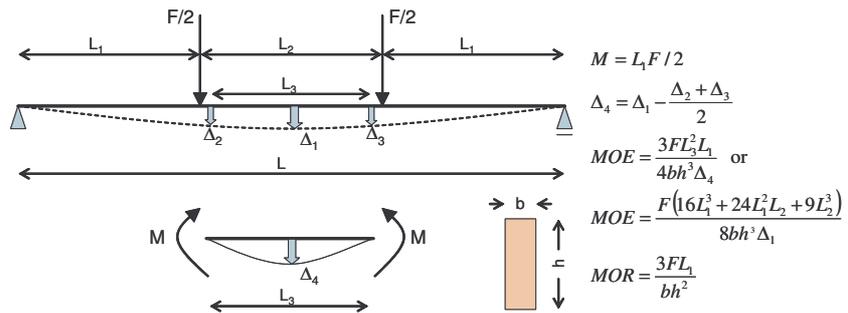


Figure 1: Test set-up to determine the modulus of elasticity in bending (MOE) and the bending strength (MOR).

In Figure 1 two different equations for the determination of the modulus of elasticity (MOE) are shown. Since the ratio $\frac{L}{h} \approx 18$, and,

consequently, the shear deformation is of minor importance, both equations can be used. In this paper Eqn. 1 is used.

$$MOE = \frac{3FL_3^2 L_1}{4bh^3 \Delta_4} \quad (1)$$

With: F	$F_{0,4} - F_{0,1}$ [N]
	defined in figure 1
Δ_4	$\Delta_{4;0,4} - \Delta_{4;0,1}$ [mm]
	defined in Figure 1
0,4	at approximately 40% of the failure load
0,1	at approximately 10% of the failure load
b	beam width [mm]
h	beam height [mm]
$L_i; L_3$	defined in Figure 1 [mm]

The bending strength (MOR) was calculated according to Equation (2).

$$\text{MOR} = \frac{3FL_1}{bh^2} \quad (2)$$

With: F load at failure
defined in figure 1

The boards were acetylated by Titan Wood using an industrial process. After acetylation and conditioning the modulus of elasticity (MOE) in bending and bending strength (Modulus of Rupture MOR) of the boards has been determined; these tests were also carried out according to Figure 1. Besides the acetylated boards, the MOE and MOR of 44 boards of untreated Radiata pine were determined. After breaking of the samples, the density and moisture content of the boards was determined by weighing and drying. Below a general flow diagram of the research program is given.

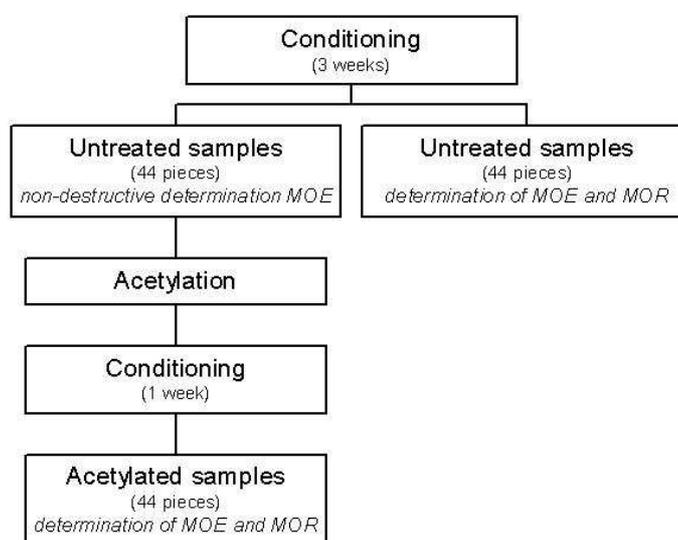


Figure 2: Test overview

RESULTS AND DISCUSSION

In Table 1, the average results of the acetylated and untreated Radiata pine are given. Due to acetylation the oven-dried density has increased by approximately 20 %, and the (equilibrium) moisture content (EMC) has been reduced from 13 to 5 %. The reduction in EMC is similar to values found in the literature, however the increase of oven-dried density is larger. Dreher *et al.* (1964) and Larsson and Tillmann (1989) found values from 7 to 10 % increase of oven-dried density. There can be some bias on these results, since the density before acetylation is determined on the whole boards, whereas the density after acetylation is determined on a small section of the board only. The modulus of elasticity in bending (MOE) of the acetylated boards stays nearly the same (averaged reduction 3 %) compared to the identical boards before acetylation.

The untreated series had a 10 % higher average bending strength (MOR) compared to the acetylated series. However, the untreated series also had a 7 % higher MOE compared to the other (not yet treated) series. Figure 6 indicates that the relation between MOE and MOR does not

change due to the acetylation process and that, consequently, the expected MOR for the untreated series is higher than for the acetylated series. On the other hand, Table 1 indicates that the variation in MOR is increased after acetylation, which, together with a slightly lower average MOR, results in a significant lower characteristic value. The characteristic value for the bending strength, based on the 44 tests carried out, for the untreated Radiata pine is approximately $f_{m;0,k} = (43-1,72*10) = 25,8 \text{ N/mm}^2$ while the characteristic value for the bending strength for the acetylated wood is approximately $f_{m;0,k} = (39-1,72*13) = 16,6 \text{ N/mm}^2$. This is caused mainly by the increased variation for the acetylated wood. This phenomenon is subject for further study, in which the type of fracture is taken into account. Another remark is that some of the boards are loaded to 71 % of their strength before acetylation instead of the intended 40 %. None of the presented values have been corrected for (equilibrium) moisture content. The reason for this is that the relationship between mechanical properties and moisture content is not known for acetylated wood, in contrast to untreated wood, for which at least some research was carried out in the past (Tsoumis 1991, Madsen 1992).

Dreher *et al.* (1964) found for Ponderosa pine and red oak a reduction in bending strength, while the modulus of elasticity in bending, or bending stiffness, remained unchanged after acetylation. Almost no change in bending stiffness and –strength due to acetylation was found by Larsson and Tillmann (1989) for small clear samples Norway spruce and Scots pine. Work of Bongers and Beckers (2003) shows that the effect of acetylation on the mechanical properties is heavily dependent on the acetylation process. The reduced EMC and increased density “upgrades” the mechanical properties. On the other side, the reduction of the amount of fibres and lignocellulose per volume (due to swelling) and possible hydro-thermal effects during the acetylation process, result in a decrease of mechanical properties.

Table 1: Average density, moisture content, bending stiffness (MOE) and bending strength (MOR) before and after acetylation (between brackets standard deviation)

Treatment	Before acetylation				After acetylation			
	Oven dried density [kg/m ³]	Moisture content [%]	MOE [N/mm ²]	MOR [N/mm ²]	Oven dried density [kg/m ³]	Moisture content [%]	MOE [N/mm ²]	MOR [N/mm ²]
Acetylated	411 (38)	13.1 (1.5)	9064 (2268)	-	492 (48)	5.2 (3.1)	8788 (2320)	39 (13)
Untreated	417 (25)	12.2 (1.3)	9664 (2130)	43 (10)	-	-	-	-

All above values are averaged results. For a better investigation of the results, and to be able to determine the effect of acetylation upon the bending stiffness and strength, individual values need to be studied. In Figure 3, the effect of acetylation upon the bending stiffness (MOE) is shown in a frequency diagram. The MOE before acetylation is defined as 100 %. In this figure, as well as in Figure 4, it can be seen that for the individual boards the tendency in MOE change is slightly negative (the regression coefficient in Figure 4 is slightly lower than 1).

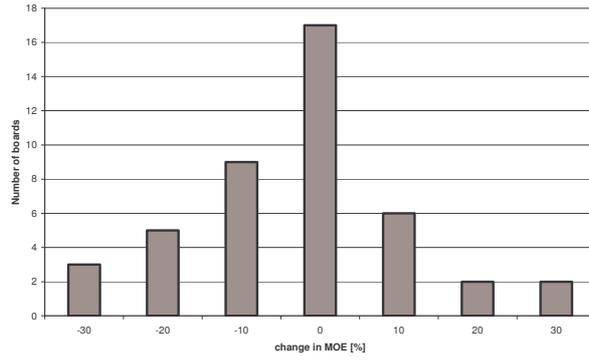


Figure 3: Change in modulus of elasticity (MOE) in bending due to acetylation

Remark:

- 30% : the absolute change is more than 25%
- 20% : the change is between -15% and -25%
- 10% : the change is between -5% and -15%
- 0% : the change is between -5% and +5%
- 10% : the change is between 5% and 15%
- 20% : the change is between 15% and 25%
- 30% : the change is more than 25%

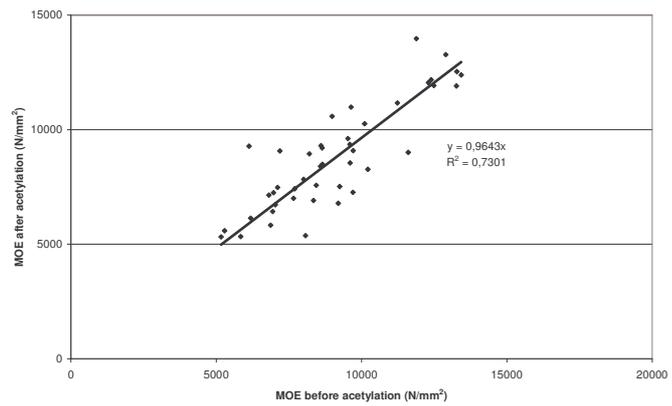


Figure 4: Bending stiffness (MOE) before and after acetylation

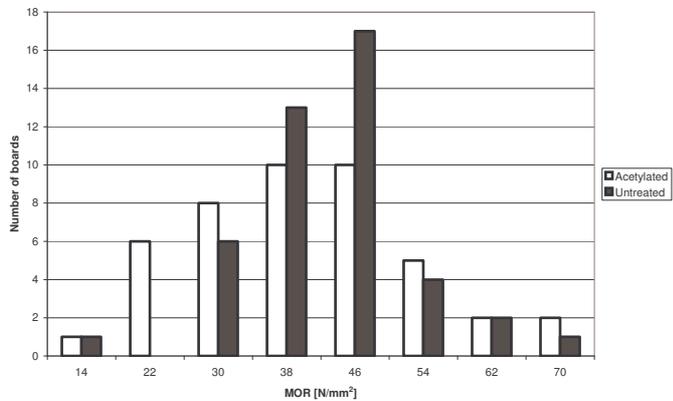


Figure 5: Frequency diagram of bending strength of untreated and acetylated Radiata pine.

In Figure 5, the distribution of the bending strength (MOR) of untreated and acetylated Radiata pine is shown. This figure shows that the distribution of the bending strength is rather scattered. Due to this scatter, an effect of the acetylation upon the bending strength (distribution) is not clearly visible. Grading and sorting of the timber before acetylation could result in a less scattered distribution and would therefore be beneficial for commercial exploitation of acetylated wood in load-bearing applications. Sorting and grading of timber before and after acetylation by (non-destructive) determination of the bending stiffness is possible, even in a mechanical way, since the relation between bending stiffness and –strength is unchanged by acetylation (see Figure 6). On the other hand the coefficient of determination (R^2) for the relation MOR-MOE for untreated Radiata Pine is so low that mechanical grading based on the relation MOR-MOE alone is not accurate enough; other parameters as knots and growth disturbances must most probably also be considered. Density does not clearly correlate with bending stiffness nor bending strength.

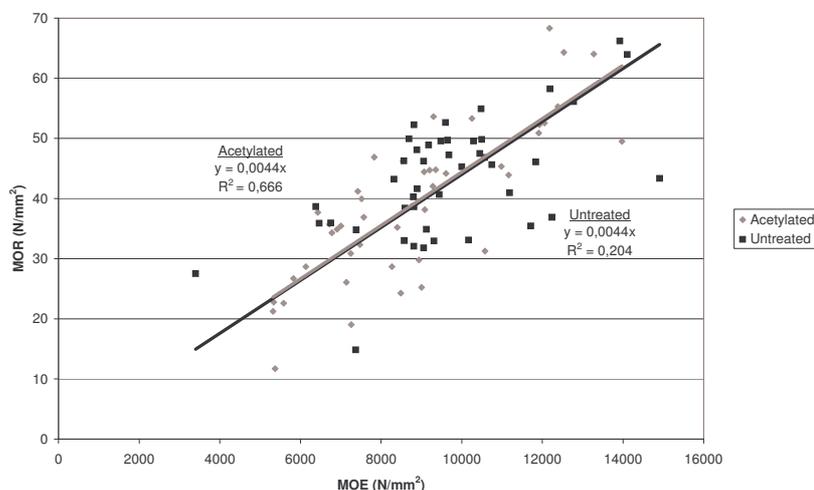


Figure 6: Relation between bending stiffness and –strength for untreated and acetylated Radiata pine

CONCLUSIONS

Acetylation of Radiata pine in structural sizes does most probably not significantly influence the modulus of elasticity (MOE) in bending negatively. The acetylation process does not alter the relationship between modulus of elasticity in bending and bending strength (MOR). The bending strength of the tested material was lower for the acetylated wood compared to the untreated wood. The mean value of MOR is only slightly lower for the acetylated material, however, due to an increase in variation, the characteristic value drops significantly. This is still subject for further research. The data will be analysed in more detail and a/o visual characteristics (knot area ratio, slope of grain, type of fracture) will be taken into account. Besides the bending stiffness and strength, further research is targeting various other mechanical properties (tensile, compression, impact bending and embedded strength) on the same material. A more thorough study of the effect of moisture content (and temperature) on the mechanical properties of acetylated wood is desirable for calculation purposes in structural engineering.

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THE EFFECTS OF CHEMICAL MODIFICATION ON THE PHYSICAL AND MECHANICAL PROPERTIES OF PARTICLEBOARDS PRODUCED FROM ALDER AND SPRUCE CHIPS

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Keywords: Chemical modification, dimensional stabilisation, particleboard, acetylation, carboxylic acid anhydrides

ABSTRACT

In this paper, it was aimed to investigate the physical and mechanical properties of modified particleboards made from spruce and alder species growing widely in the Black Sea region in Turkey. Spruce and alder chips were reacted with acetic, succinic, maleic and phthalic anhydride at a constant temperature for 3 hours. Phenol formaldehyde (PF) particleboard resin (47 % solids content) was used for manufacturing of the boards. The particleboards were produced with three layers. Mattresses were hand-formed and hot pressed at 150°C for 7-9 minutes by using a pressure of 24-26 kp/cm². Target board density was 0.65 g/cm³. Some physical properties of the particleboards, such as density, equilibrium moisture content, thickness swelling and water absorption rate as and some mechanical properties of the particleboards such as modulus of rupture (MOR), modulus of elasticity (MOE), internal bonding (IB), perpendicular screw-holding strength (PSH) and lateral screw-holding strength (LSH) as were determined. Chemical modification of boards reacted with anhydrides improved the physical and mechanical properties. The best results were determined when chips were reacted with acetic and succinic anhydride. Maleic anhydride treated boards gave the lowest values. The particleboards produced from alder chips gave better values for thickness swelling, water absorption rates, IB, MOR, MOE, PSH and LSH than those of spruce particleboards.

INTRODUCTION

It is well known that modification of wood improves the durability in an environmentally friendly way, not by toxifying but by altering the substrate. Apart from durability, properties like dimensional stability, hardness, UV-resistance and adsorption behavior can be also improved by modification. In addition, chemical modification of wood can simultaneously improve many properties of wood with a single treatment.

These improvements make wood an appropriate material in many more applications than untreated wood. In recent years, there have been studies of chemical modification to increase dimensional stabilisation, biological and mechanical resistance besides timbers on the panel products. Since 1980, in the particleboard industry there have been a lot of studies made on acetylation technology. Although there have been few papers published concerning modification of solid wood with other linear chain anhydrides (*i.e.* propionic, butyric, valeric, hexanoic anhydrides) (Stamm and Tarkow 1947, Hill and Papadopoulos 2002, Papadopoulos and Gkaraveli 2002), there has been no study dealing

with the application of chemical modification with these anhydrides in particleboard manufacture (Papadopoulos and Gkaraveli 2003). In order to fill in the gap in this area, spruce and alder chips were reacted with acetic anhydride and other dicarboxylic acid anhydrides (*i.e.* maleic, phthalic and succinic anhydrides) in this study. The aim of this research was to determine the physical and mechanical properties of particleboards manufactured from modified alder and spruce chips.

EXPERIMENTAL

Test Materials

For the production of particleboard, alder (*Alnus glutinosa*) and spruce (*Picea orientalis* (L.) Link.) wood samples were used as a raw material obtained from Trabzon, located in northern east part of Turkey. The resin (PF), which was made at 47 % solids content, 200-500 cPs viscosity, 10.5-13 pH, was provided from the Polisan Company in Türkiye. Aceton, xylen, acetic, maleic, phthalic and succinic anhydrides were obtained from chemical supplier, Merck.

Modification of spruce and alder chips

The chips were dried in an oven at 105°C to approximately 1-2 % moisture content and acetylated with acetic anhydride/xylene mixture at 120°C for 3 hours in a reaction vessel. At the end of the reaction, the chips were removed from the vessel and washed with acetone and water in order to remove the excess chemicals. Later on the chips were dried at 105°C to approximately 1-2 % moisture content, prior to board manufacture. A weight percent gain was determined based on the oven dry weight of chips. The process of succinic, maleic and phthalic anhydride treatments were similar to acetic anhydride treatment. For the succinic anhydride treatment, acetone was used as solvent and reaction temperature was 130°C. For the maleic anhydride treatment, xylen used as solvent and the reaction temperature was also 130°C. For the phthalic anhydride treatment, xylene was used as solvent and the reaction temperature was 140°C.

Particleboard manufacturing and testing

Pre-weighed raw material was placed into a resin blending chamber equipped with a rotary arm agitator. The phenol formaldehyde (PF) particleboard resin (47 % solids content) was used for the manufacturing of boards. The particleboards were produced with three layers. 10 % and 8 % resin were used for the exterior and internal layer, respectively. The total blending and mixing time were approximately 3 minutes. Mattresses were hand-formed and hot pressed at 150°C for 7-9 minutes using a pressure of 24-26 kp/cm². Target board density and thickness were 0.65 g/cm³ and 18 mm, respectively. Three replications of each board were made, yielding a total of 30 boards. After manufacturing, the boards were conditioned at 20°C and 60 % relative humidity for 4 weeks.

The density of boards (δ), equilibrium moisture content (EMC), water absorption rate and thickness swelling (TS) were determined according to EN 323/1 (1999) EN 322 (1993), EN 317 (1993), respectively.

Modulus of rupture (MOR) and modulus of elasticity (MOE), internal bonding (IB) and screw-holding strength were determined according to,

EN 310 (1993), EN 319 (1993), BS 1811 (1969) and BS 2604 (1970), respectively.

The data obtained from mechanical and physical tests were subjected to ANOVA variance analysis and a Newman Keuls's difference test in order to evaluate the significance of the modifications on the board properties.

RESULTS AND DISCUSSION

The physical and mechanical properties of the three layer experimental particleboards made from modified chips are summarised in Table 1 and Table 2, respectively. Figure 1, Figure 2 and Figure 3 shows water absorption rate, thickness swelling rate and mechanical properties for the boards produced from both alder and spruce chips, respectively.

Table 1: Physical properties for control and modified particleboards and SNK test results

Board type	Density (g/cm ³)	EMC (%)	Water Absorption (%)				Thickness Swelling (%)				
			2 hours	24 hours	48 hours	72 hours	2 hours	24 hours	48 hours	72 hours	
AA- alder	Mean	0,684(a)	6,68	60,9	65,3	68(c)	69,8	8(d)	9,3(e)	9,7	9,7
	St.d	0,03	0,47	4,77	4,76	5,12	5,15	0,70	0,75	0,85	0,86
MA-alder	Mean	0,653(b)	11,08	68,9	78,34	82,1	83,3	14,4	16,8	17,7	17,9
	St.d	0,03	0,35	8,260	8,50	8,96	8,93	2,80	2,82	3,41	3,35
FA- alder	Mean	0,666(ab)	9,10	66	77,9	79,9(b)	81(b)	15,8	19,2	19,4	19,8(b)
	St.d	0,03	0,29	4,5	4,19	4,15	4,16	1,71	1,66	1,48	1,74
SA- alder	Mean	0,669(ab)	8,08	64,3	74,62	79,5	79,4	12,4	14,6	15(d)	15,4
	St.d	0,02	0,34	5,21	5,20	5,77	5,75	1,93	2,19	2,32	2,36
Control-alder	Mean	0,663(ab)	10,26	108,9	116,08(a)	120,3(a)	121,1(a)	38,9(a)	40,5	41,1	41,1
	St.d	0,02	0,27	10,28	13,39	10,80	11,4	5,40	5,52	4,89	5,54
AA-spruce	Mean	0,709(a)	7,55	50,2	61,5	64,6	66,51	6,3	8,6(e)	8,6	9,2
	St.d	0,03	0,34	5,79	4,80	5,09	4,93	0,61	0,62	0,63	0,50
MA-spruce	Mean	0,651	9,92	100,76(b)	107,1	109,5	111,3	31,9	34,3	35,1	35,9(b)
	St.d	0,01	0,27	7,84	7,16	7,59	7,25	2,20	2,47	2,03	1,1
FA-spruce	Mean	0,649(c)	9,10	89,3	98,3	99,8	100,1	23,8	24,5	28	28,6(c)
	St.d	0,01	0,29	6,68	6,94	6,22	6,19	1,83	2,22	2,18	1,96
SA-spruce	Mean	0,678(b)	8,08	73(d)	78,4	79,6	81,3	16,4	17,7(d)	17,8	18,2
	St.d	0,02	0,34	5,16	5,30	4,89	4,80	1,17	1,24	1,14	1,26
Control-spruce	Mean	0,658(c)	10,68	109,5	115,9	117(a)	118,1	37,3	38,7	38,5(a)	39,5(a)
	St.d	0,01	0,40	8,03	8,16	7,61	7,93	2,98	3,23	3,25	2,78

*: Different letters indicate a significant difference among to groups

AA-alder: acetic anhydride treated alder particleboard

AA-spruce: acetic anhydride treated spruce particleboard

MA-alder: maleic anhydride treated alder particleboard

MA-spruce: maleic anhydride treated spruce particleboard

FA-alder: phthalic anhydride treated alder particleboard

FA-spruce: phthalic anhydride treated spruce particleboard

SA-alder: succinic anhydride treated alder particleboard

SA-spruce: succinic anhydride treated spruce particleboard

Control-alder: control alder particleboard

Control-spruce: control spruce particleboard

Table 2: Mechanical properties for control and modified particleboards and SNK test results

Board type		MOR (N/mm ²)	MOE (N/mm ²)	IB (N/mm ²)	PSH	LSH
AA- alder	Mean	12,23(b)	1586,26(b)	0,43(a)	77,20(b)	65,68(a)
	St.d	0,95	88,40	0,04	6,15	7,02
MA alder	Mean	9,40(d)	1309,18(d)	0,12(e)	51,16(e)	27,76(d)
	St.d	0,88	113,47	0,02	5,84	7,73
FA alder	Mean	15,54(a)	1779,64(a)	0,26(d)	55,40(d)	41,32(c)
	St.d	1,01	80,13	0,04	7,82	7,60
SA alder	Mean	11,36(c)	1454,54(c)	0,35(b)	59,32(c)	45,72(b)
	St.d	0,85	47,10	0,04	4,63	4,79
Control- alder	Mean	11,5(c)	1451,97(c)	0,31(c)	89,40(a)	68,28(a)
	St.d	0,84	83,52	0,03	4,10	5,98
AA- spruce	Mean	13,38(a)	1837,24(a)	0,63(a)	90,44(a)	69,16(a)
	St.d	1,11	81,29	0,04	9,85	9,40
MA spruce	Mean	11,5(b)	1274,77(c)	0,07(e)	28,76(e)	15(d)
	St.d	1,39	44,10	0,01	6,96	4,01
FA spruce	Mean	11,82(b)	1370,34(b)	0,18(d)	47(d)	40,16(c)
	St.d	1,69	34,07	0,04	5,33	6,61
SA spruce	Mean	11,68(b)	1366,12(b)	0,32(b)	69,52(b)	43,28(c)
	St.d	0,85	48,88	0,04	6,54	5,37
Control- spruce	Mean	11,42(b)	1368,40(b)	0,27(c)	59,20(c)	55,28(b)
	St.d	0,56	110,31	0,02	5,21	6,60

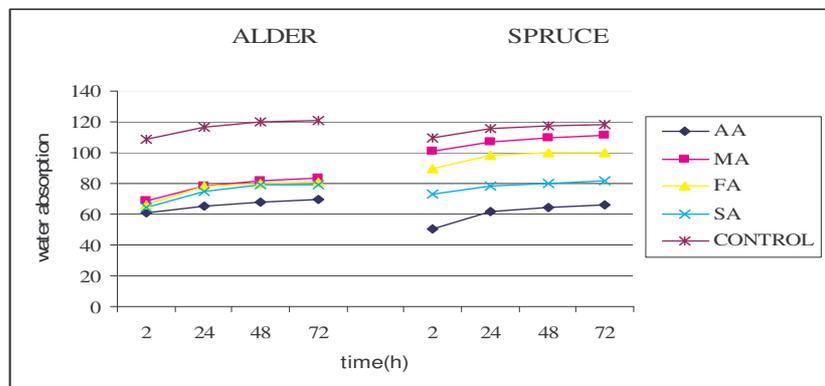


Figure 1: Water absorption rate for alder and spruce boards

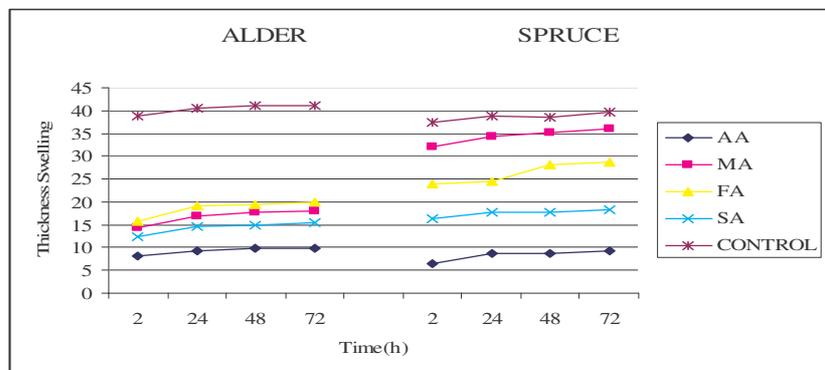


Figure 2: Thickness swelling rate for alder and spruce boards

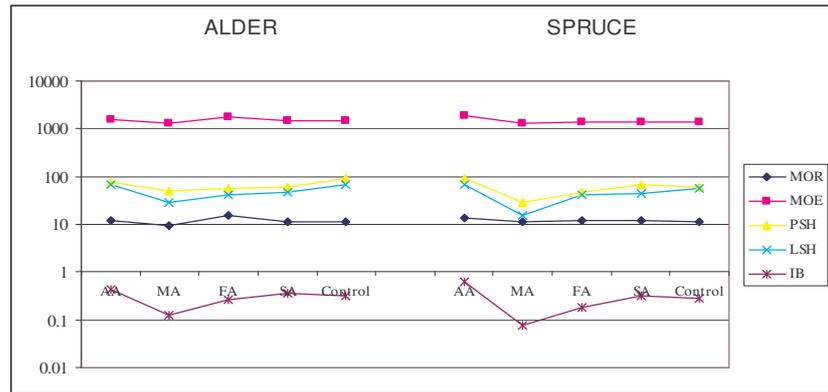


Figure 3: Mechanical properties for alder and spruce boards

As seen Table 1 and Table 2, the Newman Keuls test showed that the effect of modification treatments on physical and mechanical properties of the boards was statistically significant. The lowest density values were obtained with maleic anhydride treated boards but the highest density values were determined with acetic anhydride and then in succinic anhydride treated boards. The highest equilibrium moisture contents were obtained with control boards then maleic anhydride treated boards for spruce boards; with maleic anhydride treated boards for alder boards. Acetic and succinic anhydride treated boards gave the lowest values.

As seen Figure 1 and Figure 2, all the modified boards decreased thickness swelling and water absorption rate. Particleboards produced from alder chips gave better values for TS and water absorption rates than particleboards produced from spruce chips. The order in maximum decreased water absorption rate and TS values were maleic anhydride < phthalic anhydride < succinic anhydride < acetic anhydride.

MOR and MOE values were higher when acetic anhydride was used for boards produced from spruce chips and when phthalic anhydride was used for boards produced from alder chips than others. Maleic anhydride treated boards gave the lowest MOR and MOE values for both of them. Acetic and succinic anhydride treated boards gave the best internal bonding values, while maleic anhydride treated boards gave the lowest values. Perpendicular screw-holding strength (PSH) and lateral screw-holding strength (LSH) values were higher control boards for alder, acetic anhydride for spruce boards than others. Maleic anhydride treatment gave the lowest values like other mechanical properties (Figure 3). Maximum IB, PSH, LSH values were found to be maleic anhydride < phthalic anhydride < succinic anhydride < acetic anhydride.

The maximum thickness swelling (24 h) requirement EN 312-4 (1996) is 15 %. Acetic and succinic anhydride treated alder boards and acetic anhydride treated spruce boards met the required level given in the standard.

MOR values ranged from 9.4 to 15.54 N/mm². MOR requirement for general purpose boards by EN 312-2(1996) is 11.5 N/mm². Except for maleic anhydride treated alder boards, all of the other boards had similar MOR values with the related standards. Phthalic anhydride

treated boards can be used for interior fitments (including furniture) (EN 312-3, 1996).

The range of data in modulus of elasticity was from 1274.77 to 1837.24 N/mm². MOE requirements are 2000 N/mm² for general purpose boards, 1600 N/mm² for interior fitments (including furniture). None of the boards had the required level of modulus of elasticity for general purpose. Phthalic anhydride treated alder boards and acetic anhydride treated spruce boards had the required level of MOE for interior fitments (including furniture) (EN 312-2, EN 312-3, 1996).

Internal bond data ranged from 0.078 to 0.635 N/mm². The minimal requirement of internal bond for general purpose boards by EN 312-2 (1996) is 0.24 N/mm². Except for maleic anhydride treated boards and phthalic anhydride treated spruce boards, all of the other boards had higher internal bond than the general purpose requirements.

Chemical modification of the chips with some anhydrides used in this study improved the density and decreased the equilibrium moisture content of the particleboards. In other words, physical and some mechanical properties were higher than control boards. Cell-wall modifications result in lowering of cell-wall moisture content and the fiber saturation point; thus, mechanical properties of modified wood are reported to improve, probably due to lowering of cell-wall moisture (Homan *et al.* 2000, Brelid and Simonson 1999). The lowest density and highest equilibrium moisture content values were obtained with maleic and phthalic anhydride treated boards. Acetic and succinic anhydride treatment increased density and decreased moisture content; therefore, the boards treated with these anhydrides improved the physical and mechanical properties.

Reaction with phthalic and maleic anhydride didn't yield durable ester bonds (Kumar 1994). For this reason, these anhydrides may not give good values for physical and mechanical properties. Low rates of water absorption, TS, IB, PSH, LSH of maleic and phthalic anhydride treated particleboards may be attributed their low pH values because the pH values of maleic and phthalic anhydride were 2.49 and 2.56, respectively. In addition, the acidic properties of chips, resulting from maleic and phthalic anhydride treatments, can interact with the alkaline properties of phenol formaldehyde (PF) and this interaction could increase the gel time and affect the internal bonding. For the good adhesion, pH must be 4-5 (Haygreen and Bowyer 1985). Maleic anhydride is known to cause more acidic and hydrophilic conditions than succinic anhydride (Mahlberg *et al.* 2001). Due to the acidity of the chips, this anhydride may give lower mechanical and physical properties than succinic anhydride. Succinic and phthalic anhydride are used for production thermo-moldable products commonly (Hassan *et al.* 2000). Phthalic anhydride is used for producing PVC/cellulosic fiber composites (Matuana *et al.* 1998). In this study, phthalic anhydride gave a very good MOE and MOR values. This may be due to a plasticity reaction between phthalic anhydride and wood with high temperature. For the phthalic anhydride treatment, reaction temperature was 140°C. High temperature increases the elasticity (Hills and Rozsa 1978).

Mahlberg *et al.* (2001) reported that modification of wood fibers with maleic anhydride resulted in a reduction in the modulus of rupture of PF and PF/PP-bonded boards, whereas acetylation and modification with

succinic anhydride didn't cause any significant changes in the MOR of the boards. Dimensional stability of the fiber boards was observed to increase significantly as result of the modifications. Among the anhydrides, acetic and succinic anhydride decreased the TS values more than maleic anhydride. Modified boards gave higher IB values than controls.

CONCLUSIONS

In this study; chemical modification of wood chips treated with acetic, maleic, succinic and phthalic anhydride improved the dimensional stability of particleboards. Results showed that TS and water absorption rate values for modified boards were much lower than controls. Among the esterification treatments, the increments of thickness swelling and water absorption values of treated particleboards with acetic and succinic anhydrides were greater than those of the others. This indicated that the dimensional stability of chips treated with these anhydrides were better than that treated with the other reagents, such as maleic and phthalic anhydride.

Mechanical properties were affected by particleboard's density, equilibrium moisture content, wood species and pH values. According to the test results except for MOR and MOE, all of other mechanical properties were higher in acetic and succinic anhydride treatments than in other treatments. But phthalic anhydride had positive effect on MOR and MOE.

The particleboards produced from alder chips gave better values than particleboards produced from spruce chips. The wood species showed different effects on physical and mechanical properties. The reason for that may be due to their anatomical differences, resin and pH values. For modified particleboards, giving the improved properties related with reaction time and temperature so depends on WPG.

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PERFORMANCE OF COATINGS ON ACETYLATED SCOTS PINE AFTER MORE THAN NINE YEARS OUTDOOR EXPOSURE

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Keywords: Scots pine sapwood, acetylation, coatings, outdoor exposure

ABSTRACT

Acetylation of wood is known to enhance especially the durability and dimensional stability of the wood. A reduction of 70-80% of swelling / shrinkage can be obtained. This reduction is beneficial for the durability of wood coatings due to a more stable substrate. This results in a decreased maintenance frequency.

Acetylated and untreated Scots pine panels, coated with white, black opaque and teak pigmented transparent alkyd and acrylic coatings, have been evaluated after more than 9 years of outdoor exposure.

The panels were evaluated after 5½, as well as after 9½ years exposure, with regard to the degree of blistering, cracking, flaking and chalking. After 9½ years additionally, the adhesion has been determined under wet and conditioned circumstances. The coating layer thickness and biodegradation by fungi was evaluated.

After 9½ years exposure, the coating of the reference panels was severely cracked and flaked, or in some cases even no coating layer was present anymore. Furthermore all reference panels are in bad condition due to wood rot.

Compared to the reference panels, the acetylated panels have a remarkably better performance. Especially the acrylic white opaque coating is still in good condition.

INTRODUCTION

Acetylation with uncatylsed acetic anhydride has been studied extensively the past decade and has shown to considerably improve the durability and dimensional stability of a wood species (Beckers *et al.* 1998, Beckers and Militz 1994, Beckers *et al.* 1994, Goldstein *et al.* 1961, Larsson-Brelid *et al.* 2000, Militz 1991, Rowell *et al.* 1989, Singh *et al.* 1992).

Less swelling and shrinkage of wood results in less stress on a coating, which enhances durability of the coating system on exterior used wood (De Meijer, 2002), and thereby decreases the maintenance frequency.

In this research, the durability of commercial waterborne and solvent borne coatings, both opaque and transparent, has been investigated in an outdoor exposure test. The coatings were applied on acetylated and untreated Scots pine sapwood, and exposed during 9 years to natural weathering. The results of a visual inspection of the coating layer after 5½ years of outdoor exposure were presented during the First European

Conference on Wood Modification in Ghent (Nienhuis *et al.* 2003). In this paper the results after 9½ years outdoor exposure are reported.

EXPERIMENTAL

One-meter long boards of Scots pine sapwood (*Pinus sylvestris* L.) were acetylated (envelope treatment) in a small-scale pilot plant. After removing the residual acetic acid the boards were cross cut to 300 mm length, and coated in two layers of 40 to 50 µm each with the following coatings:

- 1 Transparent teak coloured alkyd (solvent based)
- 2 Transparent teak coloured acrylic (water based)
- 4 Opaque white acrylic (water based)
- 5 Opaque black acrylic (water based)
- 6 Opaque white alkyd (solvent based)
- 7 Opaque black alkyd (solvent based)

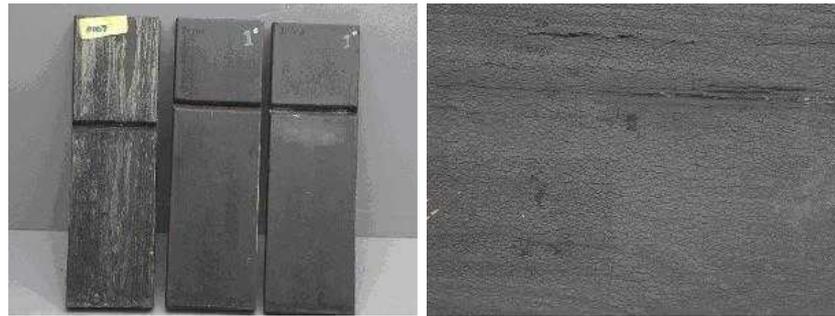
The coated panels (10 x 80 x 300 mm) were exposed since September 1995 at the exposure site of SHR Timber Research, Wageningen, the Netherlands. Panels were placed on a rack facing south in an angle of 45°. Part of the acetylated samples contained 3 to 4 % residual acetic acid, while the other acetylated samples were totally free of residual acetic acid. As a reference, untreated Scots pine sapwood panels were coated and exposed. Before exposure, some panels were damaged by artificially applied hail.

The coating systems have been evaluated after 9½ years of outdoor exposure with regard to the visual aspects; blistering, cracking, flaking, chalking (ISO 4628 series) and mould growth (EN 927-3). In this period, there has been no maintenance whatsoever of the coating system. The adhesion of the coating (according to ISO 2409) and layer thickness (microscopy) was determined as well.

RESULTS AND DISCUSSION

Figure 1 shows the panels after 9½ years of outdoor exposure. Summarising, it can be said that most untreated samples have hardly any coating left, or the coating is severely damaged (cracking / flaking). The condition of the coatings on acetylated wood was remarkably better, when compared to the coatings of the untreated samples. There was not much difference between acetylated, acetylated with residual acetic acid and hailed or non-hailed samples.

The transparent coatings (alkyd / acrylic) showed a degradation of the coating itself. On the acetylated samples the acrylic opaque coatings, and especially the white coloured coating, showed the best results after the outdoor exposure.



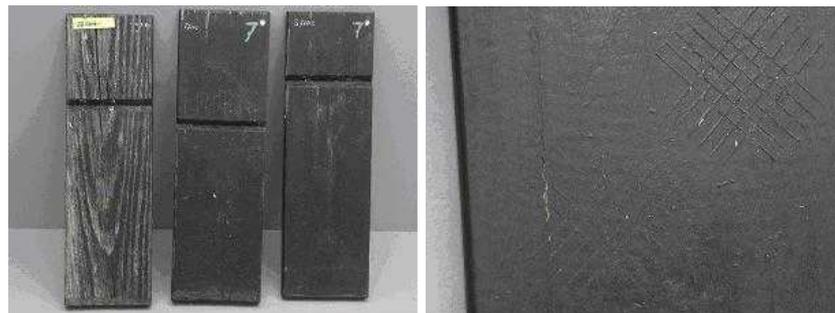
Transparent teal coloured alkyd

Degradation of coating itself



Opaque white acrylic

Opaque white alkyd



Opaque black alkyd

Adhesion of an opaque dark alkyd coating on acetylated Scots pine

Figure 1: Performance of coatings after 9½ years of outdoor exposure

For most untreated wood samples, the adhesion could not be determined because almost no coating was left on the surface. Remarkably better adhesion was found for the acetylated samples compared to the untreated samples. In general, the acrylic coatings on acetylated wood showed the best adhesion. In Figure 2, two photographs of adhesion tests of untreated and acetylated coated with an opaque white acrylic coating are given.

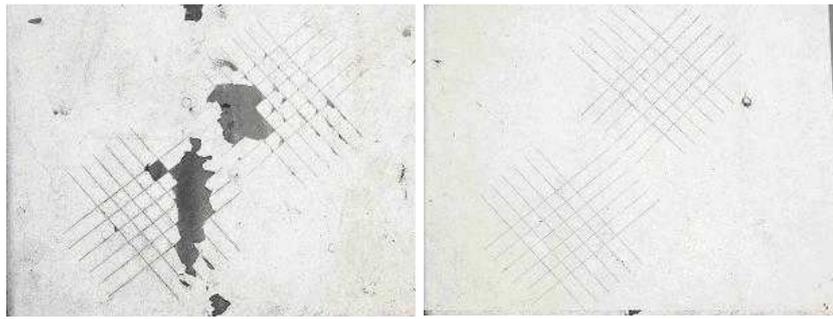


Figure 2: Adhesion test (ISO 2409) under wet conditions of untreated (left) and acetylated coated with an opaque white acrylic coating after 9½ years of outdoor exposure

CONCLUSIONS

Acetylated wood has a significantly better result with respect to long term coating performance compared to untreated wood. After 9½ years outdoor exposure, untreated samples had seriously cracked and flaked coating systems, and in some cases the coating was even completely eroded. The adhesion of the coating after 9½ years outdoor exposure on acetylated wood is still good. This is valid under both dry and wet conditions. The intrinsic quality of the coating itself has become the main factor affecting the durability of coatings on acetylated wood. With an acrylic opaque white coating, the condition of the coating after 9½ years without any maintenance was still good. If a coating system is adapted to be used on acetylated wood and the application is done in the appropriate way, it is expected that the maintenance frequency can be once every ten years or even longer.

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A STUDY ON THE PROPERTIES OF COMPOSITES MADE FROM ACETYLATED SAWDUST AND WASTE CELLULOSE ACETATE

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Keywords: Acetate anhydride, Cellulose acetate, Esterification, Extractive, Modulus of rupture, Thickness swelling, Water absorption.

ABSTRACT

In this investigation, composites were made from acetylated pine wood sawdust and waste cellulose acetate. The effects of wood extraction, esterification and cellulose acetate content on the dimensional stability and mechanical properties of composites were studied. The pine wood sawdust was esterified by using acetic anhydride without a catalyst to an ester content of 14 % WPG. The properties of composites, such as bending strength, water absorption and thickness swelling were studied and compared with control samples. The results showed that extraction and esterification had a positive effect on these properties. Increasing the amount of cellulose acetate decreased the water absorption and thickness swelling; while, the maximum modulus of rupture was achieved at a cellulose acetate content of 10 %.

INTRODUCTION

During recent years, technology has been developed to produce new composites of waste lignocellulosic materials. Thermoplasticisation of waste lignocellulosic materials is one possible method to effectively utilise unused woods, such as thinned woods and sawdust. Several studies have been reported concerning the thermal softening of lignocellulosic materials. Funakoshi *et al.* (1979) reported that esterification affects the thermoplastic properties of wood. Matsuda (1987) prepared esterified woods by addition reactions of wood with dicarboxylic acid anhydrides in the presence or absence of a solvent such as dimethyl formamide. Gomez-Bueso *et al.* (1999) acetylated lignocellulosic fibers of different origins and then laboratory fibre boards were produced from the acetylated fibres by using powdered phenolic resin of the novolak type as a binding agent. Control boards made from unmodified fibres were also produced. The results showed that acetylation improved the mechanical properties of fiberboards. Hassan and Rowell (2000) esterified bagasse fiber by using succinic anhydride (SA) in the absence of solvent, and used scanning electron microscopy to prove the occurrence of thermo-plasticisation of the esterified fibers. Mohammadi-Roshandeh (2003) plasticised poplar wood by benzylation and acetylation.

Cellulose acetate is one of the cellulose derivatives that are produced from the reaction of acetic acid, acetic anhydride and sulphuric acid on alpha cellulose. Cellulose acetate has many uses in areas such as the acetate fibers, film and plastic industries and for use in cigarette fibers. Waste cellulose acetate is produced by the tobacco industries. The objectives of this study were to use the waste cellulose acetate in sawdust particle binding and study the effects of wood extraction and esterification on composite properties.

EXPERIMENTAL

Pine (*Pinus* spp) sawdust passed through mesh 40-60 was used as the filler. The sawdust extractive materials were extracted with a 1 % NaOH solution. The esterification followed a procedure that was described by Matsuda (1987). About 10 g of sawdust was placed in a 250 ml beaker and acetic anhydride (150 ml) was added as reagent with 0.2 g of Na_2CO_3 as catalyst. The mixture was stirred for 4 h at 80°C. Thereafter, acetone was added to the mixture and it was filtered to separate the product. The esterified wood was washed in acetone and subsequently with distilled water. Afterwards, it was extracted with acetone for 6 h in a Soxhlet to remove un-reacted acetic anhydride and then dried in an oven at 100°C. The achieved weight percent gain (WPG) was calculated based on Equation 1.

$$\text{WPG (\%)} = (W_2 - W_1) / W \times 100 \quad (1)$$

Where: W_1 = initial weight of sawdust (g)
 W_2 = weight of esterified sawdust (g)

A metal frame (22x15x1cm) was made and then the acetylated sawdust (50 g) was placed in the frame and hot-pressed (180°C with a load of 30 kg/cm²) for 10 min to make a board.

Three factors were considered as statistical variables as follows:

- 1) Waste cellulose acetate at three percentages of 0, 10, 20 % (based on oven-dry weight).
- 2) The presence or absence of extractives.
- 3) Esterification at two levels (esterified and non-esterified).

Other manufacturing factors were considered as constants; specific gravity (1.2 g/cm³), adhesives (phenol formaldehyde, 5% based on oven dry weight of sawdust), press time (5 min), temperature (180 °C), board thickness (2.5 mm). Three boards were manufactured for each combination of the variables.

Data were analysed were statistically by using factorial design at probability levels of 95 and 99 % (or $\alpha = 0.05$, $\alpha = 0.01$). Grouping of the averages was analyzed by a Duncan Multiple Range Test (DMRT) when analysis of variances (ANOVA) showed statistical differences.

RESULTS AND DISCUSSION

The results of cellulose acetate content, wood extraction and esterification on the modulus of rupture (MOR), water absorption, thickness swelling of composites are shown in Tables 1, 2, and 3 respectively.

Table1: Effect of cellulose acetate content on the MOR, water absorption and thickness swelling.

Cellulose acetate [%]	MOR [kg/cm ³]	24-hr water absorption [%]	24-hr thickness swelling [%]
0	159.5	37.59	16.17
10	303	28.45	10.25
20	175.5	25.12	7.24
Prob.	**	**	**
C.V.(%)	12.6	7.5	4.95

**significant at level of 1%

Table 2: Effect of wood extraction on the MOR, water absorption and thickness swelling.

Samples	MOR [kg/cm ³]	24-hr water absorption [%]	24-hr thickness swelling [%]
Unextracted	180.83	31.56	12.82
Extracted	244.5	29.21	9.62
Prob.	**	**	**
C.V (%)	12.6	7.5	4.95

**significant at level of 1%

Table 3: Effect of wood esterification on the MOR, water absorption and thickness swelling.

Samples	MOR[kg/cm ³]	24-hr water absorption [%]	24-hr thickness swelling [%]
Non-esterified	186	34.19	12.67
Esterified	239	26.58	9.77
Prob.	**	**	**
C.V (%)	12.6	7.5	4.95

**significant at level of 1%

As indicated in Table 1, increasing the cellulose acetate content up to a value of 10% increased MOR. Increased cellulose acetate content decreased water absorption and thickness swelling after 24h immersion. The effect of cellulose acetate content on MOR, water absorption and thickness swelling after 24h immersion is significant at a level of 1 %. This influence is positive for water absorption and thickness swelling with increasing of cellulose acetate. However, the highest MOR was achieved at 10 % cellulose acetate content. Table 2 shows that extraction of sawdust materials improved MOR, water absorption and thickness swelling after 24 h immersion and is statistically significant at level of 1%. Non-tannin extractive materials such as glucose and hydrocolloid gums have a negative effect on adhesion and also their hydroxyl groups can absorb water, therefore increasing water absorption and thickness swelling. Table 3 shows the effect of esterification of sawdust upon MOR, water absorption and thickness swelling after 24 h immersion. Esterification increased MOR due to an increased thermoplasticity of particles, associated with a decreased water absorption and thickness swelling and consequently improved dimensional stability.

Figure 1 shows the effects of cellulose acetate content, wood extraction and esterification that are statistically significant on the MOR at a probability level of 1%. This shows that MOR was increased by particle extraction and esterification, and with increasing cellulose acetate content up to 10 %.

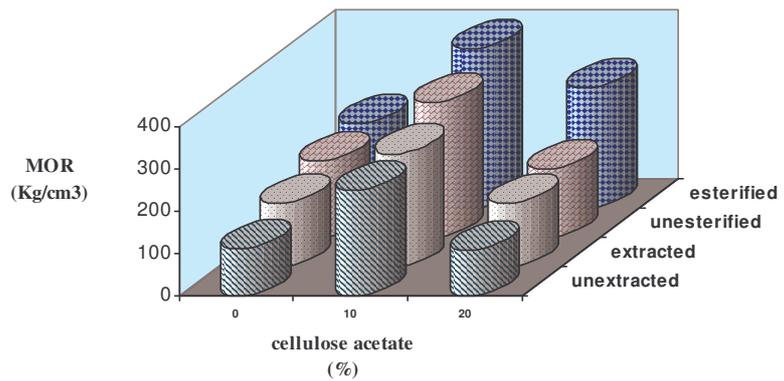


Figure 1: Effects of cellulose acetate content, wood extractive materials and esterification on the MOR

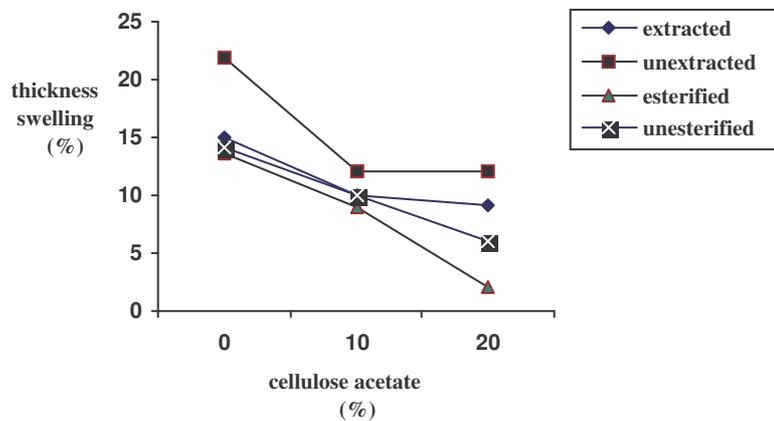


Figure 2: Effects of cellulose acetate content, wood extraction and esterification on the thickness swelling

Figure 2 shows the effect of extraction and sawdust esterification and increasing cellulose acetate content upon thickness swelling. Three factors are statistically significant at level of 1 %. There are different reports about esterification effects on the MOR. Rowell (1990) reported no statistical differences in modulus of rupture was found between acetylated and non-acetylated boards.while Gomez-Bueso (1999) and Hassan (2000) showed esterification increased MOR. However, those authors believed that esterification decreased water absorption and thickness swelling.

CONCLUSIONS

Generally, wood extraction and esterification have positive effects on the dimensional stability and mechanical properties of composites. An increase of cellulose acetate content reduced the water absorption and thickness swelling. In this study, the maximum modulus of rupture was gained at a cellulose acetate content of 10 %.

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DIMENSIONAL STABILITY OF CHIPBOARD MADE OF WOOD CHIPS ACETYLATED WITH ACETIC ANHYDRIDE

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Keywords: Acetylation, Scots pine wood chips, chipboard, dimensional stability

ABSTRACT

Changes in chipboard dimensions occurring by air humidity changes influence substantially the behavior of constructions with chipboards. Possibilities of increasing chipboard dimensions stability by standard methods like waterproofing by using petrochemical substances are limited. In the Wood Technology Institute in Poznań, Poland, an investigation on the modification of wood chips with acetic anhydride has been launched. Scots pine wood chips, before being coated with MUPF resin, were acetylated with liquid acetic anhydride at 130°C for 3 hours. After that, chipboards were made of acetylated and dried chips. Among other issues, changes of board dimensions resulting from air humidity changes were investigated. It has been found that acetylation greatly increased waterproof properties of chipboards and as a result dimensional stability within the plane perpendicular to the surface. It has also been determined that acetylation did not increase chipboard resistance to hot water and hot steam.

INTRODUCTION

The question of dimensional stability of chipboards and other wood-based materials is vital from the perspective of their application in construction. Changes in board dimensions occurring due to air humidity changes influence substantially the behaviour of constructions with chipboards. Much research has looked at the possibilities of increasing chipboard dimensional stability, but only by simple technology modifications, *i.e.* modifications which do not need large technology changes, or a substantial increase in production costs, are limited. For instance, through increasing the degree of glue resin coating, which makes adhesive-bonded joints of relatively high resistance to water (MUPF, PF, MDI). A conclusion was drawn that in order to increase the wet dimensional stability of chipboards, it is necessary to apply more effective methods for reducing hydrophilic properties. One of the possibilities of reducing wood affinity for water is acetylation, that is substitution of acetyl groups [CH₃CO-] for hydroxyl groups [-OH]. In the Wood Technology Institute in Poznań research was therefore undertaken to determine the possibilities of increasing dimensional stability of Scots pine wood chipboards through their acetylation with acetic anhydride.

EXPERIMENTAL

Laboratory produced flat cut Scots pine wood chips (*Pinus sylvestris*) of the average dimensions of: length: 20±10 mm, width: 5±2.5 mm, thickness: 0.4±0.2 mm were subjected to acetylation with acetic anhydride. The reaction was conducted in the liquid environment with the following technological parameters:

- temperature: (130±5)°C,
- time of heating to a temperature of 130°C: 0.5 h,
- time of carrying out the reaction in the anticipated temperature: 3 h,
- time of cooling down to 30°C: 1 h,
- weight proportions of reagents: 1:10 (chips dry mass : acetic anhydride).

Single-layer boards of the nominal thickness of 12 mm and density of (700±30) kg/m³ were made of acetylated chips and for the purposes of comparison with non-acetylated chips. A resin of the MUPF type was used to bond the chips. The amount of the resin applied was 10 % in relation to the chips dry mass. Additional waterproofing agents were not applied. Appropriate samples were taken from the produced boards and among other things the following properties were tested:

- dimensional stability according to the EN 318 standard,
- thickness swelling and length after soaking in water according to the EN 317 standard,
- thickness and length swelling after conducting the aging test according to the ASTM D 1037:93 standard,
- thickness and length swelling after conducting the aging test according to the EN 321 standard,
- mechanical properties of boards subjected to strength tests according to the EN 310 and EN 319 standards.

RESULTS AND DISCUSSION

Table 1: Some properties of single-layer boards of Scots pine wood chips – acetylated and non-acetylated – covered with the MUPF resin

Test type	Unit of measurement	Type of chips		Scots pine wood ¹⁾
		non-acetylated	acetylated	
equilibrium moisture content	%	9.7	4.6	12.3
thickness swelling (2h of soaking in water)	%	18.5	1.0	4.0 ²⁾
thickness swelling (24h of soaking in water)	%	20.7	3.5	5.5 ²⁾
absorbability (2h of soaking in water)	%	63.3	12.4	48.5
absorbability (24h of soaking in water)	%	73.8	39.9	66.6
thickness swelling (1h of boiling in water)	%	34.7	28.6	–
absorbability (1h of boiling in water)	%	113.0	91.9	–
thickness swelling (change RH from 35 % to 85 %)	%	6.7	1.6	2.4 ²⁾
length swelling (change of RH from 35 % to 85 %)	%	0.15	0.12	0.12 ²⁾
thickness swelling (test acc. to the EN 321)	%	18.5	3.8	Not tested
thickness swelling (test acc. to the ASTM D 1037:93)	%	32.1	43.8	
bending strength (EN 310)	N/mm ²	26.6	20.1	
tensile strength (EN 319)	N/mm ²	0.45	0.46	
tensile strength (EN 319 after a test acc. to the EN 321)	N/mm ²	0.15	0.37	
tensile strength (EN 319 standard after a test V100)	N/mm ²	0.12	0.08	

1) samples: 50 mm x 50 mm x 12 mm

2) in tangential direction

3) along the fibers

The chosen test results are presented in Table 1. According to the expectations the waterproof properties of boards made of acetylated chips was greater than these of the boards used for comparison. Their waterproof properties were also higher than those of solid pine wood. The equilibrium moisture content (EMC) of boards of acetylated chips indicates their relatively low affinity for water and moisture. In a normal atmosphere (65%/20°C) the EMC was 4.6 % and was two times smaller than that of boards of non-acetylated chips and 2.5 times smaller than that of pine wood. The amount of water absorbed by the soaked samples of boards of modified chips was several times lower than in the case of boards of non-modified chips.

The results of the aging test according to the EN 321 standard, indicate the potentially higher resistance of boards of acetylated chips compared with boards of non-acetylated chips to the destructive action of atmospheric factors. Lower swelling of these boards after the tests contributed to less loosening of their structure and as a result less deterioration of mechanical properties. Tensile strength of the boards made of modified chips decreased by less than 20 %, but in the case of boards of non-modified chips it decreased as much as by 67 %. Bending strength decreased by 31 % and 50 %, respectively. However, test results of the strength tests that are more demanding than the test according to EN 321, *i.e.* V100 test and the test according to ASTM D 1037, do not support these observations.

CONCLUSIONS

Acetylation of Scots pine wood chips with acetic anhydride greatly increases their waterproof properties.

Thickness stability of boards made of Scots pine wood chips can be increased through acetylation of the chips with acetic anhydride.

Dimensional stability in the plane of boards made of Scots pine wood chips is not significantly influenced by acetylation of the chips with acetic anhydride.

Dimensional stability in the plane of chipboards is close to the stability of pine wood along the fibers.

Acetylation of Scots pine wood chips with acetic anhydride does not increase chipboard resistance to hot water and hot steam.

WATER REPELLENT EFFECT OF THE ACETYLATION ON POPLAR FIBRES

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Keywords: acetylation, EMC, IR-spectroscopy, moisture repellent effect, Poplar fibre, *Populus nigra* L.

ABSTRACT

Fibres of poplar wood (*Populus nigra*) were prepared and oven dried. Afterwards, they were acetylated with acetic anhydride without a catalyst. Acetylation was carried out for different duration at 120°C. Different weight percent gains (WPGs) were achieved based on the operated conditions. Acetylated fibres were exposed to varying relative humidity to determine equilibrium moisture contents (EMC). IR-spectra were also taken from the fibres to indicate substitution of the hydroxyl groups with the acetyl groups. Results showed that the acetylation decreased moisture absorption in the fibres. It was revealed that a WPG of about 10% had a proper water repellent effect on fibres. IR-spectra confirmed properly the substitution of the acetyl groups.

INTRODUCTION

Any change in the chemistry of wood cell wall polymers affects the physical and mechanical properties of the wood, or composites made from the wood. These properties can vary from color change to major changes in modulus properties, strength, gas permeability, moisture sorption and water repellence, bioresistance and dimensional stability in wood and wood-based composites such as fibreboards, particleboards, *etc.*

Acetylation is a type of chemical modification by which hydroxyl groups on the cell wall polymers are substituted with acetyl groups from acetic anhydride (Goldstein *et al.* 1961, Rowell 1983, Mohebbi 2003, 2005). Changes in the moisture sorption of the wood fibre cell walls have a major effect on the mechanical properties and dimensional stability of fibreboard as well as its bioresistance (Takahashi *et al.* 1989, Militz 1991, Chow *et al.* 1996, Fuwape and Oyagade 2000, Ohmae *et al.* 2002). At moisture contents between oven dry to the fibre saturation point, any changes in the moisture content will affect the major properties of the fibreboard. Hydroxyl groups on the fibre cell wall polymers are responsible for moisture sorption. Substitution of the hydroxyl groups with acetyl groups can be used to improve the technological properties of the fibreboard (Rowell 1996).

Current research has studied the acetylation of poplar fibres, which is a commonly used wood species in Iran, using acetic anhydride. The moisture sorption and water repellent properties of the fibres before the board manufacture have been investigated.

EXPERIMENTAL

Fibre preparation

Poplar (*Populus nigra* L.) chips were prepared by using a laboratory chipper (Pallman 430x120). They were sieved to achieve uniform sizes (2x20x25mm). They were then dipped in water for few hours and steamed at 175°C for 5 minutes. Steamed chips were refined by using a laboratory single disk refiner. Refining was carried out five times. The fibres were subsequently oven dried at 103±2°C for 24 hours.

Acetylation

Dry fibres were weighed and placed in aluminium capped beakers and the acetylation reaction was carried out for 0, 30, 60, 90, 120, 150, 180, 360 and 2520 minutes at 120°C under atmospheric pressure, using acetic anhydride without a catalyst. The acetylated fibres were rinsed in water to remove the acetic acid and excess acetic anhydride until no acid smell was detected. The washed fibres were oven dried at 103±2°C for 24 hours and weighed to determine their weight percentage gains (WPGs) (Eqn. 1).

$$\text{WPG (\%)} = (W_{\text{act}} - W_{\text{od}}) / W_{\text{od}} \times 100 \quad (1)$$

Where:

WPG = Weight Percent Gain (%)

W_{act} = Dry weight after acetylation (g)

W_{od} = Dry weight before acetylation (g)

IR-spectroscopy

Attenuated Total Reflection (ATR) Infrared Spectroscopy was carried out to prove the acetylation reaction with the fibres. A few milligrams of the oven-dried acetylated fibres were put on a detector prism and IR spectra were collected directly from the fibres by using a FTIR Bruker Vectra 22 equipped with a DuraSample IR II™ detector. Background spectra were collected by using an empty detector. Sample and background spectra were collected using 60 scans at a spectral resolution of 4cm⁻¹. A rubber band method was used for the baseline correction. The band for CO₂ was excluded to make a suitable baseline correction (Mohebbi 2003, 2005).

Equilibrium Moisture Content (EMC)

About 3 grams of the acetylated and non-acetylated fibres were placed in a climate chamber with varying relative humidity at 25°C. At certain relative humidities, the equilibrium moisture content (EMC) of the fibres was calculated. Based on the EMCs, the water repellent efficiency (WRE) of the acetylation was calculated for the acetylated fibres (Eqn. 2).

$$\text{WRE (\%)} = (\text{EMC}_{\text{non}} - \text{EMC}_{\text{act}}) / \text{EMC}_{\text{non}} \times 100 \quad (2)$$

Where:

WRE = Water Repellent Effect at certain relative humidity (%)

EMC_{non} = Equilibrium Moisture Content of non-acetylated fibres (%)

EMC_{act} = Equilibrium Moisture Content of acetylated fibres (%)

RESULTS AND DISCUSSION

The WPGs of the acetylated fibres are shown in Figure 1. Results revealed that rate of the acetylation reaction in the fibres followed an exponential trend. It was higher during the first hours of the reaction and a weight gain of 10% was achieved after 120min at an atmospheric pressure without any catalyst; while, achieving higher WPGs required a longer time. For example, a weight gain of 18% was achieved after 42 hours (Fig. 1).

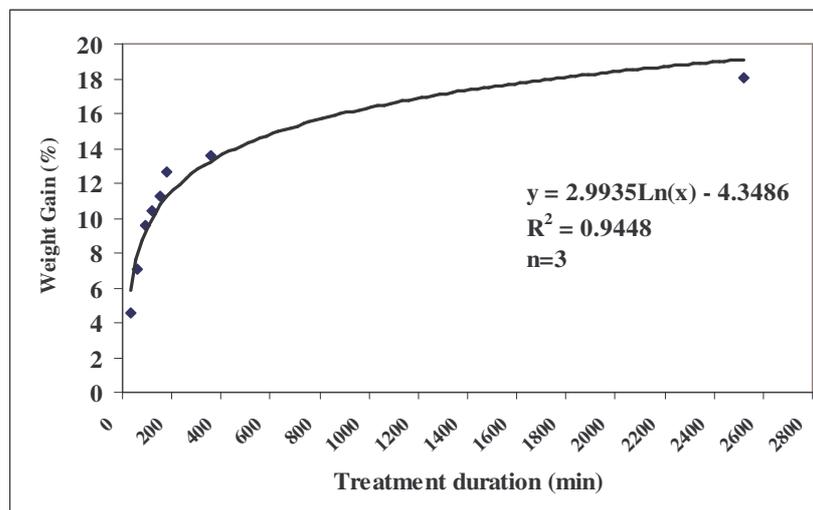


Figure 1: Weight gains of non-catalysed acetylation in the Poplar fibres at an atmospheric pressure

IR spectra of the acetylated fibres are shown in Figure 2. It was revealed that at wave numbers between $3500\text{--}3300\text{cm}^{-1}$ (1) the intensities were decreased due to the acetylation. This peak has been assigned for OH stretching of absorbed water to the cell wall polymers (Fengel and Wegner 1980, Pandey and Theagarjan 1997, Pandey 1999, Mohebbi 2005). The magnitude of the peak was increased at higher WPGs. This indicates that the number of OH groups was decreased due to the substitution of the acetyl groups during the acetylation in the fibre walls. It is well known that acetylation improves water repellence in wood due to a decrease in the number of OH groups (Rowell 1983).

A peak that is assigned for CO_2 (2), was increased at 2358cm^{-1} at higher WPGs. This peak was excluded from the spectra during the base line correction and it was not considered in this research.

There were prominent peaks in the finger print region ($1800\text{--}600\text{cm}^{-1}$) where their intensities were increased due to the acetylation at raised WPGs. An assigned peak (3) at wave number 1730cm^{-1} is related to un-conjugated C=O stretch in xylan (Takahashi *et al.* 1989, Sundell *et al.* 2000, Pandey and Pitman 2003, Mohebbi 2003, 2005). The intensity of this peak was increased at higher WPGs in the fibres (Fig. 2). This peak shifted slightly to higher wave numbers ($1730\text{--}1739\text{cm}^{-1}$) in the acetylated fibres (Table 1). Another peak (4) at 1363cm^{-1} , has been assigned to C-H deformation in cellulose and hemicelluloses, increased due to the acetylation (Evans *et al.* 1992, Pandey and Theagarjan 1997, 1999, Chang *et al.* 2000, Mohebbi 2003, 2005). Its intensity was also increased at higher WPGs in the poplar fibres. A prominent peak (5) at 1236cm^{-1} increased due to the acetylation. This peak has been assigned

to C-O stretching and C=O deformation in lignin and xylan (Faix 1991, 1996, Faix and Böttcher 1992, Pandey and Pitman 2003, Mohebbi 2005). Its intensity increased at higher WPGs. This peak slightly shifted to other close wave numbers (1226-1236 cm^{-1}) due to the substitution of the acetyl groups (Table 1). The peak has slightly been shifted to lower wave numbers at higher WPGs.

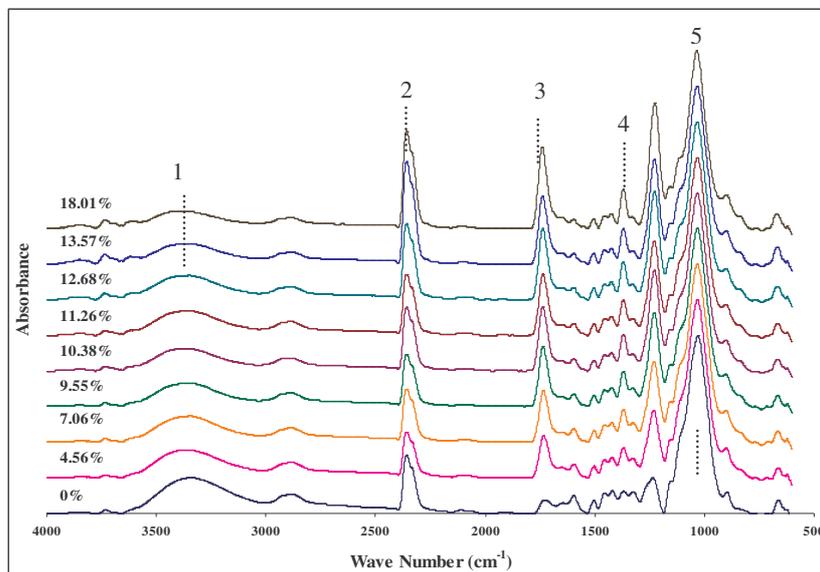


Figure 2: IR-spectra of the acetylated Poplar fibres

Results indicated that the acetylation affected the moisture sorption of the poplar fibres and it was decreased by raised WPGs (Fig. 3). A decreased moisture sorption was rated as high at higher relative humidities than lower ones. Study on the WRE of fibres due to acetylation showed that this property was increased by raised WPGs with same rates at different relative humidities (Fig. 4). Results revealed that the acetylation had higher rate of WRE at WPGs below 10% and about 50% of WRE was achieved in this range. However, increased rate of the WRE was slowed down at higher WPGs.

Table 1: Wave numbers and their assignments in the acetylated poplar fibres

Peak number	Weight Percent Gain (%)								Assignments	
	Non-acetylated	4.56%	7.06%	9.55%	10.30%	11.20	12.60%	13.50%		18.01%
1	3352	3359	3344	3348	3352	3350	3350	3340	3390	OH stretching (bonded) ¹
2	2358	2358	2358	2358	2358	2358	2358	2358	2358	C=O stretching due to presence of carbon dioxide
3	1730	1731	1733	1735	1737	1735	1735	1737	1739	C=O stretching in acetyl groups, increased due to acetylation in xylan ^{2,3}
4	1363	1363	1363	1363	1363	1363	1363	1363	1363	C-H deformation in CH ₃ from acetyl groups due to acetylation in hemicelluloses and cellulose ^{4,5,6,7}
5	1236	1232	1230	1228	1228	1228	1226	1226	1226	Stretching of C-O and C=O deformation in the ester bond formed during acetylation ^{6,8,9}

1. Fengel and Wegner (1983); 2. Takahashi et al. (1989); 3. Sundell et al. (2000); 4. Evans et al. (1992); 5. Pandey and Theagarjan (1997, 1999); 6. Pandey and Pitman (2003); 7. Chang et al. (2000); 8. Faix (1991 and 1996), Faix and Böttcher (1992)

CONCLUSIONS

From the current study, it could be concluded that the fibres react with the acetic anhydride and a substitution of the hydroxyl groups with the acetyl groups occurs versus the time. The reaction was proved by IR spectroscopy. A moderate and an efficient acetylation occur at first minutes when the reaction proceeds. Any increased the WPG affects the moisture sorption and the water repellence in the fibres. The moisture sorption decreases when the WPG increases. The water repellent effect of the acetylation increases when the WPG arises. Consequently, an improvement of dimensional stability in manufactured products could be expected when the WPG increased in the fibres.

ACKNOWLEDGEMENTS

We would express our sincere thanks to Dr. Carsten Mai, Institute of Wood Biology and Wood Technology, Göttingen University, for his great cooperation in taking IR spectra from the fibres.

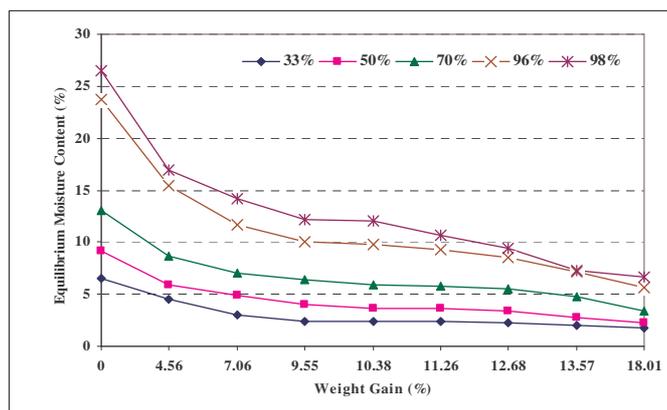


Figure 3: Equilibrium moisture content (EMC) in the acetylated Poplar fibres

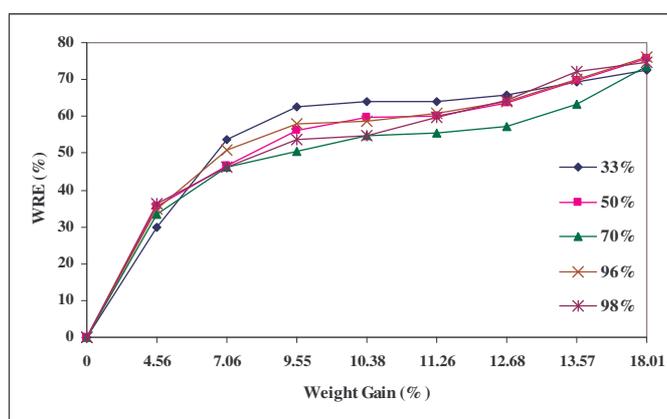


Figure 4: Water Repellent Effect (WRE) of the acetylation on the Poplar fibres at different relative humidities

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SMOKE ANALYSIS OF ACETYLATED BEECH LAYERS

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Keywords: Acetylation, beech layer, smoke, CO₂, CO, C_xH_x, O₂, anti-Swelling-efficiency, swelling, bulking effect

ABSTRACT

Layers of Oriental beech (*Fagus orientalis*) were prepared in sizes of 50 × 50 × 2 mm³. The specimens were acetylated with acetic anhydride without a catalyst at 120°C for varying durations to achieve different weight gains (WPGs). Bulking effect of the acetylation was measured on thickness of the layers. Anti-Swelling-Efficiency (ASE) was determined in the acetylated layers after 2 and 24 hours of dipping in water. Thereafter, the layers were oven dried and then evolved smoke gases from the layers were analysed by using a portable gas analyzer on a burning hot plate. It was revealed when the WPG increased; the bulking effect in the beech layer thicknesses was raised due to the acetylation. At the highest WPG (17.8 %), the highest bulking effect (3.79 %) and the highest ASE (96 %) were determined. The acetylation decreased the thickness swelling in layers dipped in water for 2 and 24 hours with 0.27 % and 0.31 % respectively. Gas analysis of the formed smoke revealed that the acetylation decreased carbon monoxide and C_xH_x as 37 % and 31.58 % respectively at WPG of 17.8 %. However, CO₂ was increased as 50 % after burning of the layers with 17.8 % of WPG. Oxygen consumption was negligibly changed due to the acetylation.

INTRODUCTION

Wood products should be gained some important technical properties to be accepted for commercial markets. Technologically, those products should have appropriate mechanical strengths, dimensional stability, bioresistance, fire resistance *etc.* Acetylation is now known as one of the modification processes, which increases mechanical strength, dimensional stability and bioresistance in wood and lignocelluloses. Of course, some mechanical properties are also reduced due to the acetylation; however, they achieve the standard levels normally.

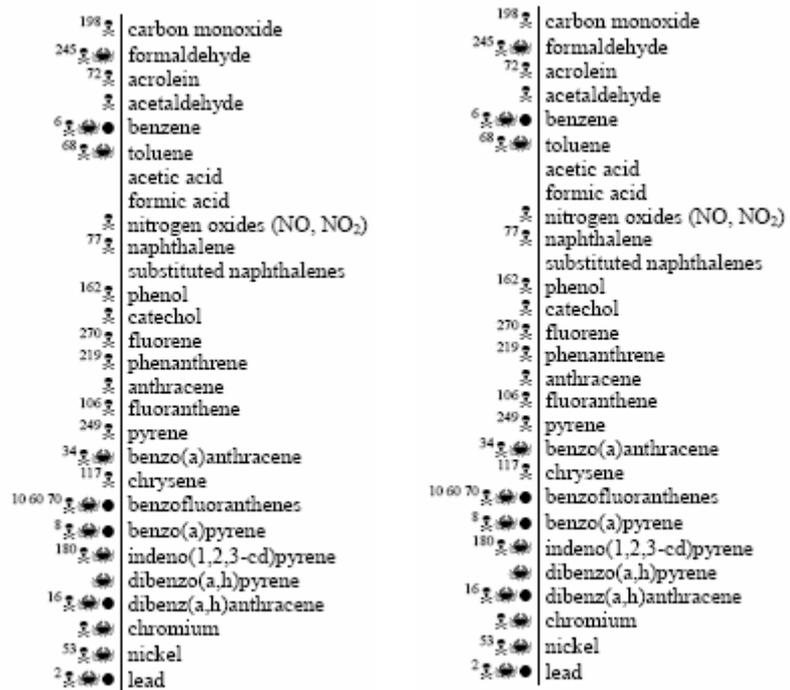
Many researches have been done in the field of acetylation; such as bioresistance (Mohebbi 2002, 2003a, b, Militz 1991, Becker and Militz, 1995), mechanical properties (Rowell *et al.* 1988, Mahlberg *et al.* 2001, Fuwape and Oyagade 2000), dimensional stability (Militz 1991, Rowell *et al.* 1989); however no reports have been published about the influence of the acetylation on fire resistance.

Wood fire generates a number of combusive products which are known or suspected as carcinogenic agents (Burning Issues 2003). Different toxic gases are emitted from wood, normally threat human health; especially during the fire accident (Burning issues 2003). For example carbon monoxide (CO) is a colourless, odourless, tasteless and a toxic gas, which is produced by the incomplete combustion. Carbon

monoxide produces physiological effects on people, who are exposed to the concentrations shown in Table 1 (Carbon Monoxide Kills Campaign Web site 2003).

Table 1: Concentration of CO and its physiological effects

Concentration of CO in air (ppm)	Inhalation time and toxic developed
50	Safety level as specified by the health and safety executive
200	Slight headache within 2-3 hours
400	Frontal headache within 1-2 hours, becoming widespread in 3 hours
800	Dizziness, nausea, convulsion within 45 minutes, insensible in 2 hours



☠ Indicates a hazardous chemical for which ATSDR has prepared a toxicological profile
 ★ Indicates a chemical classified as a carcinogen by the US government
 ● Indicates a chemical that is one of the Top 20 CERCLA priority hazardous substances
 1-275 Indicates position on the CERCLA priority hazardous substances list

Figure 1: Chemicals found in wood smoke (Burning Issues 2003)

Carbon monoxide poisons by entering the lungs *via* the normal breathing mechanism and displacing oxygen from the bloodstream. Interruption of the normal supply of oxygen puts at risk the functions of the heart, brain and other vital functions of the body organs with the highest oxygen requirement. It reversibly binds haemoglobin, resulting in relative anaemia. Because it binds haemoglobin 230-270 times more avidly than oxygen small concentrations can result in significant levels of carboxyhaemoglobin (HbCO) (E-Medicine 2005, National Safety Council 2005). Very high levels of emission during the fire cause death in human. For this reason improvement of fire resistance of the wood and lignocellulosic products are of great importance.

Carbon dioxide is also a colourless, non-flammable, non-explosive gas can threat health at toxic levels (5000 ppm) higher than that of CO, it can cause suffocation by reducing oxygen available for breathing. Breathing very high concentrations of this gas can cause lightheadedness, giddiness, shortness of breath, muscular tremors and weakness, acrocyanosis, also unconsciousness or even death (Berkley Lab 2005). During the wood combustion, some carcinogenic compounds are also produced (Simoneit *et al.* 2000) (Fig. 1). Those compounds are carbon-hydrogen based and produced due to pyrolytic process during burning in fire (Browne 1958, Tillman *et al.* 1981).

At the moment, a research is being carried out to investigate thermal behaviour and fire resistance of the acetylated beech layers and plywood. This paper presents a part of the current study on smoke analysis in the acetylated beech layers to monitor the influence of the acetylation on emitted toxic gases

EXPERIMENTAL

Acetylation

Layers of Oriental beech (*Fagus orientalis* Lipsky) with sizes of 2 × 50 × 50 mm³ were prepared and oven dried to reach an equal moisture contents. Five points were marked on the layers prior to drying. Oven dry weight of the layers was determined and their thicknesses were measured at the marked points. Thereafter, the layers were placed in beakers containing preheated acetic anhydride. The beakers were covered with Al-foil and heated at 120°C for different periods to achieve various degrees of the acetylation. Acetylated layers were washed in rinsed water to remove the excess of acetic acid. Afterwards, the acetylated layers were dried at 103±2°C overnight. Oven dried weight of the acetylated layers were determined. Weight gain percentage (WPG) of the layers was calculated based on the Equation 1.

$$\text{WPG (\%)} = (W_{\text{act}} - W_{\text{od}}) / W_{\text{od}} \times 100 \quad (1)$$

Where: WPG= Weight Percent Gain (%), W_{act} = Dry weight after acetylation (g), W_{od} = Dry weight before acetylation (g).

Bulking effect

Thickness of the layers were measured at the marked points to determine the bulking effect of the acetylation (Eq. 2).

$$B (\%) = (t_{\text{act}} - t_{\text{od}}) / t_{\text{od}} \times 100 \quad (2)$$

Where: B= Bulking effect of acetylation (%), t_{act} = Thickness of oven dried acetylated layer (mm), t_{od} = Thickness of oven dried layer (mm).

Anti-Swelling-Efficiency (ASE)-

The dried acetylated layers were soaked in water and kept at room temperature. Their weights and thicknesses were determined after 2 and 24 hours. Anti-swelling- efficiency (ASE) of the acetylation were determined based on the Equation 3.

$$ASE (\%) = (S_{non} - S_{act}) / S_{non} \times 100 \quad (3)$$

Where: ASE= Anti-swelling-efficiency of acetylation (%), S_{non} = Swelling of non-acetylated layer (%), S_{act} = Swelling of acetylated layer (%)

Smoke analysis

The acetylated layers were placed on a burning electric hot plate and an aluminium pipe (dia. 10cm) was set on top of the layer to exhaust smoke, which was emitted from the layers during the pyrolysis. The Gas Analyzer Emicont 70 - Zambelli srl was set up to collect any emitted gases from the layers to determine CO, CO₂ etc. (Fig. 1). Smoke suction was started after 15 seconds of placing the layers on the burning plate and it was lasted for 1 minute. Thereafter, calibration was carried out by using fresh air for 3min. For each WPG, six samples were used as replicates.

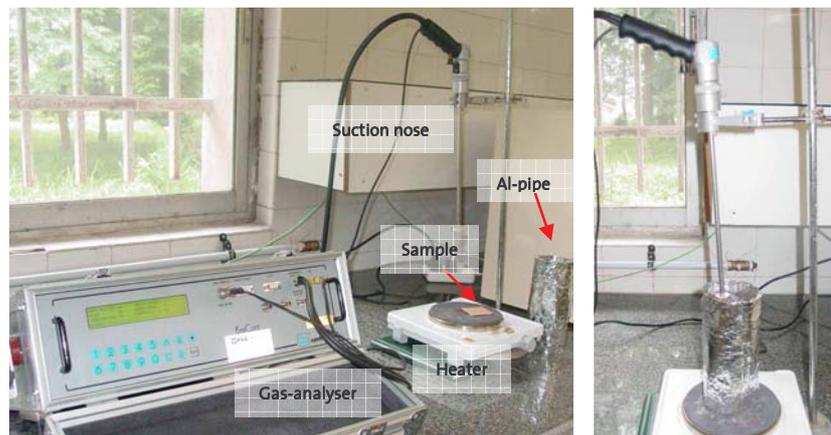


Fig. 1: A set up for smoke analysis (left) and collecting emitted gases through exhausting pipe (right)

RESULTS AND DISCUSSIONS

Acetylation

The weight percent gains (WPGs) that were achieved during the non-catalysed acetylation of beech layers under normal atmospheric pressure are presented in Table 1. Results revealed that rate of the acetylation reaction in the layers followed an exponential trend. Higher rate of the acetylation was occurred during the first hours of the reaction and a weight gain of 9 % was achieved after 30 min; while, achieving the higher WPGs required quite longer time with a slow reaction rate (Fig. 2).

Table 1: Achieved weigh gains in acetylated layers

Reaction time (min)	Weight gain (%)
15	1.24
30	9.01
60	11.49
90	13.15
1020	17.81

A bulking effect of the acetylation was revealed during the reaction. It was determined that thickness of the layers was increased due to raised WPG (Fig. 3). The highest bulking (3.79 %) was occurred at the WPG of 17.8 %.

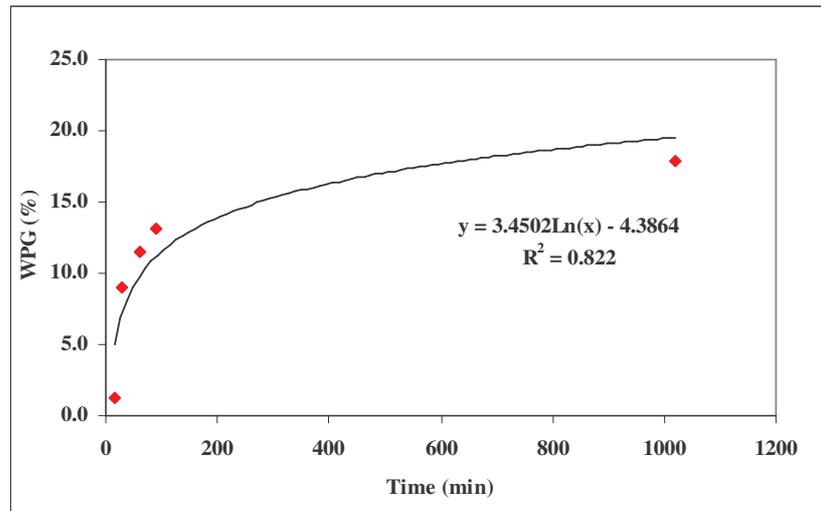


Figure 2: Acetylation kinetics of beech layers

Results also indicated that the acetylation decreased considerably thickness swelling in beech layers after soaking in water for 2 and 24 hours (Fig. 4). It was determined that the reduction rate of the swelling was rapid at WPGs below 9 %; while it was slowed down at WPGs above 9 %.

Anti-swelling-efficiency (ASE) of the acetylation on beech layers is shown in Fig. 5. Results indicated that the acetylation increased ASE in the layers. It was determined that the major decreased thickness swelling and increased ASE were occurred at WPGs lower than 9 %.

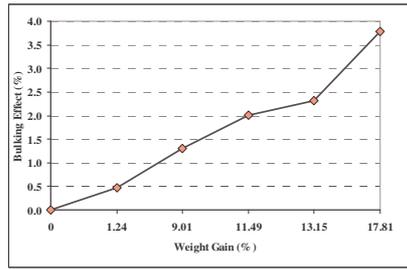


Figure 3: Bulking effect of the acetylation on beech layers

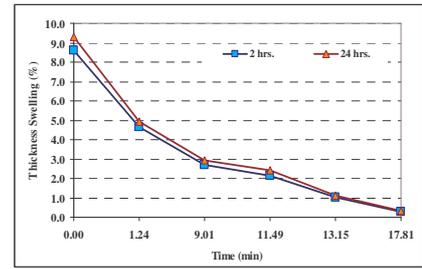


Figure 4: Swelling of the acetylated beech layer after 2 and 24 hours soaking in water

Smoke analysis

Carbon monoxide and carbon dioxide are toxic gases that are emitted during wood combustion. Analysis of CO indicated that it was influenced due to the acetylation and decreased at raised WPGs (Fig. 6). Figure 7 represents percentage of reduction in CO emission due to the acetylation. It indicates that the acetylation reduced CO emission more than 40 % in comparison with the non-treated layers.

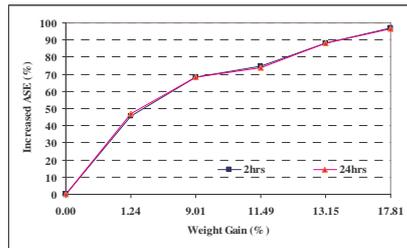


Figure 5: Anti-Swelling-Efficiency (ASE) of the acetylation on beech layers

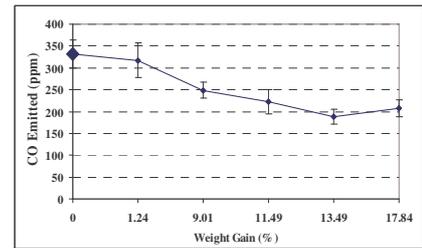


Figure 6: Carbon monoxide emission from the acetylated beech layers

It was also revealed that the CO₂ was influenced by the acetylation (Fig. 8). Results showed that the CO₂ was increased due to raised WPGs. C_xH_x represents carbon-hydrogen bearing components; such as carbohydrates. Results showed that C_xH_x was influenced by the acetylation (Fig. 8). Results showed that the acetylation increased about 50 % of the CO₂ emission (Fig. 9); while it decreased more than 30 % of the C_xH_x formation (Fig. 10).

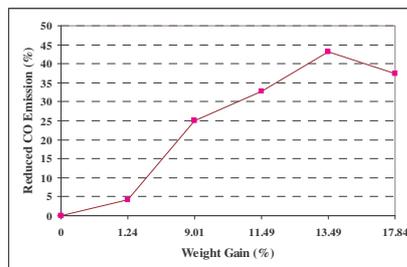


Figure 7: Decreased percentage of carbon monoxide emission from the acetylated beech layers

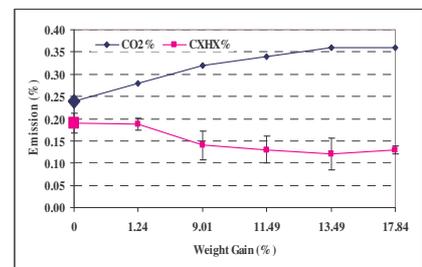


Figure 8: Emitted CO₂ and C_xH_x from acetylated beech layers

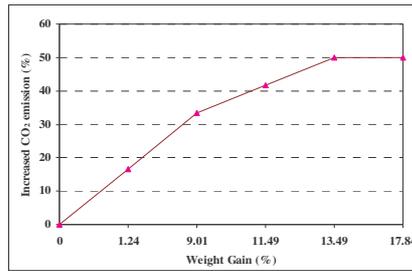


Figure 9: Increased percentage of emitted carbon dioxide from the acetylated beech layers

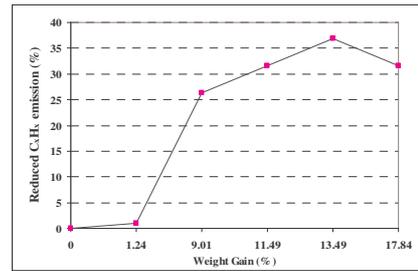


Figure 10: Decreased percentage of C_xH_x emission from the acetylated beech layers

Analysis of O₂ consumption showed that the acetylation slightly reduced O₂ when WPG was raised; however it looked insignificant (Fig. 11).

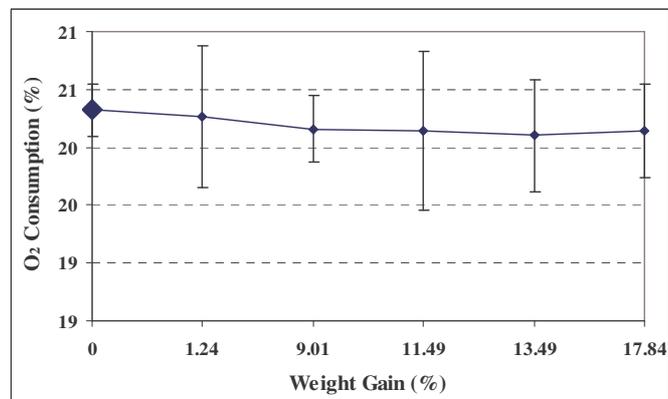


Figure 11: Consumed O₂ in acetylated beech layers

DISCUSSION

Acetylation

Based on the results, reaction of the acetic anhydride was decreased due to increased substitution of the acetyl groups in cell wall polymer. Cellulose is a polyhydroxy polymer and is a major responsible in the acetylation of wood than lignin and hemicellulose. As cellulose is encrusted by lignin (a polymer with less hydroxyl groups) and hemicellulose; any substitution of the acetyl groups occurred in lignin and the hemicellulose results lower weight percent gains in the wood. Due to the acetylation of both polymers and production of bounded adducts in microfibrils, access to cellulose polymers requires more energy and time. Therefore, acetylation of the accessible polymers (lignin and hemicelluloses) occurs at lower WPGs and acetylation of cellulose at higher WPGs. Rosenqvist (2001) reported that distribution of the acetyl groups increases by raised WPG in cell walls. Ohkoshi *et al.* (1997a, b) reported that lignin and hemicellulose are acetylated at lower WPGs than cellulose. Results also showed that an increased bulking occurred by raised WPGs. Bulking of the wood can be related to increased acetyl groups in the cell wall. Rosenqvist (2001) reported that number of the acetyl group increases by raised WPGs. Jose-Villalon-Robells (2001) and Sander *et al.* (2003) have reported bulking effect of the acetylation in softwoods and beech.

Presence of the acetyl groups increases hydrophobicity of the wood. When such hydrophobic acetyl groups substitute with hydrophilic hydroxyl groups; it could be expected that wood achieves a higher dimensional stability due to higher acetylation. As results indicated in this research, ASE was increased by raised WPGs. This research supports previous works that have reported that the acetylation increases dimensional stability in wood (Militz 1991, Hon 1996, Larsson-Brelid and Simpson, 1999, Kumar 1994, Rowell *et al.* 1989, Fuwape and Oyagade 2000, Mahlberg *et al.* 2001).

Smoke analysis

Studies of Browne (1958) indicated that hemicelluloses evolve more gases, less tar and much aqueous distillate as formed from cellulose. Pyrolysis of hemicelluloses splits C-O bonds and leads to acetic acid production and perhaps formaldehyde or carbon monoxide and hydrogen. Also a dehydration process yields furfural and other furan derivatives.

Pyrolysis of cellulose evolves water by a dehydration process in the first stage of thermal decomposition before any other significant changes. However, reports show that cellulose triacetate evolves acetic acid instead of water and fails to yield water even when pyrolysis is completed (Browne 1958). A deacetylation process might be occurred instead of the dehydration in cellulose.

Carbon-oxygen (glycosidic) bonds are expected to break at random points along the cellulose chain in early stage of pyrolysis. Cellulose can also easily hydrolysed at these points, especially in the presence of acids, which are produced during formation of acetic acid from hemicelluloses. Cleavage of glycosidic linkages sequences with glucose units formation that are bearing reducing ends. Formed glucose can dehydrate to β -glucosan (1,2-anhydroglucose) and it rearranges to β -glucosan or levoglucosan (1,6-anhydroglucose). Levoglucosan and β -glucosan are unstable and pyrolyse to water, acetic acid, formic acid, carbon dioxide, carbon monoxide, glycolic acid, furaldehyde, furan and phenols. At higher temperatures, carboxyl groups of formed acids yield carbon dioxide, a non-flammable flame inhibitive gas, whereas, aldehyde groups yield formaldehyde and then hydrogen and carbon monoxide, a highly flammable mixture.

Lignin mainly produces char and evolves gases. The aromatic units in lignin produce phenols, xylenols, guaiacols, cresols and catechols and straight chain part produces carbon dioxide, hydrocarbons, formic acid, acetic acid, higher fatty acids, the methanol that are all carbon-hydrogen based (C_xH_x) compounds. Concerning the explanation above about the chemistry of combustion in non-acetylated wood, a deacetylation process could be expected in treated woods instead of dehydration. Due to deacetylation in the cell wall polymers (hemicelluloses, cellulose and lignin), acetyl groups could be formed during the thermal degradation. These groups could change to acetic acid and some carboxyl bearing acids that are responsible for hydrolysis. Those acids yield carbon dioxide in wood. As it is expected that number of the acetyl groups are increased at raised WPG; it could be suggested that more acetic acid are formed at increased WPGs. Consequently, more hydrolysis should be expected, which results more carbon dioxide. Therefore, any increased CO_2 at raised WPGs can be related to the higher number of the acetyl groups. Reports also showed that cellulose

triacetate (acetylated cellulose) evolves acetic acid instead of water and fails to yield water even when pyrolysis is completed (Browne 1958). Reducing end groups in glucose (or cellulose) are mainly responsible for aldehyde formation. Aldehyde groups yield carbon monoxide during the combustion (Browne 1958). A deacetylation process might cease formation of aldehyde groups in glucose. Therefore, absence of aldehyde groups might sequence with a decreased carbon monoxide in the acetylated wood at raised WPGs. The presence of acetyl groups in lignin also shifts the combustion reaction to produce acetic acid or other carboxyl bearing acids in stead of other compounds. Those acids are responsible for carbon dioxide formation in wood. Therefore, any decreased C_xH_x based compounds in wood might be related to increase of acid instead.

Analysis of O_2 indicated insignificant changes of its percent in sucked smoke. However, its decrease might be related to active reaction of acetic acid or carboxyl bearing acids that were liberated from acetylated wood.

CONCLUSIONS

We can here conclude that acetylation gives a better dimensional stability to beech layers and decreases toxic and flammable gas emission (carbon monoxide) from wood during the combustion. And also it can be suggested that the acetylated wood inhibits flame propagation due to increased CO_2 , which is an inflammable gas.

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ACETYLATION OF PHOTO-THERMALLY TREATED WOOD

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Keywords: Acetylation, colour, photo-thermal treatment

ABSTRACT

This study investigated the change in colour of acetylated wood by photo-thermal treatment and the effect of acetylation on photo-thermally treated wood. The colour of acetylated wood was stable against light, however, heat treatment after light-irradiation made it change greater. Furthermore, acetylated wood discoloured greater than unacetylated by light-irradiation after photo-thermal treatment. These results show that the ACETYLATED wood is not stable when it is exposed under special conditions. On the other hand, the ΔL^* and Δa^* of wood acetylated after photo-thermal treatment were remarkably changed by light-irradiation. This result shows that acetylation is unsuitable for colour stabilisation of photo-thermally treated wood.

INTRODUCTION

There are many reports on the acetylation of wood for improving the colour stability. Feist *et al.* (1991) reported that acetylation was effective to prevent the degradation of lignin and hemicellulose of wood during accelerated weathering. Plackett *et al.* (1992) reported that the colour of the acetylated wood was stabler than that of untreated in weathering using water spraying. Ota *et al.* (1996, 1997) stated that the colour of acetylated kiri (*Paulownia tomentosa* Steud.) changed to bright pale brown after light-irradiation. Furthermore, Ohkoshi (2002) showed that the colour of acetylated softwood changed less than that of untreated one by exposure to light up to 1000 hours.

On the other hand, we reported the change in colour by photo-thermal treatment (Mitsui *et al.* 2001, Mitsui 2004). The colour changes in the heated wood after exposure to light was greater than those in unirradiated one. Furthermore, the colour of specimens irradiated for a long time changed greater than that for short time. This method is effective for coloration of wood because of no VOC emission such as toluene and xylene from paint, and less damage such as cracking and bending by treatment. However, it is questionable whether the colour obtained by photo-thermal treatment is stable against light or not.

For improvement in the colour of the surface of the wood treated by this method, acetylation was applied.

EXPERIMENTAL

Materials

This study examined the sapwood of Japanese cypress (*Chamaecyparis obtusa*) and beech (*Fagus crenata*). The samples were stored, before and between treatments, in a desiccator, in total darkness, over P₂O₅, at

room temperature. The colour parameters of Japanese cypress and beech before treatment were (L^* , a^* , b^*) = (83.09 ± 1.56 , 2.43 ± 0.13 , 20.01 ± 0.32) and (67.10 ± 0.64 , 6.46 ± 0.10 , 19.98 ± 0.35), respectively.

Acetylation

The dried specimens were treated with acetic anhydride in the liquid phase without a catalyst for 6 hours at 120°C. At the end of the reaction, the specimens were fully washed with water and dried over P₂O₅, at room temperature.

Photo-thermal treatment

Specimens were irradiated with artificial sunlight from a xenon lamp at 180 Wm⁻², in the range of 300 – 400 nm, for up to 50 hours, at 63°C (black panel) and 50 % RH, in a commercial chamber (SX-75: Suga Test Instruments Co. Ltd., Tokyo, Japan). After light-irradiation, specimens were treated in humid conditions at 90°C and 90 % RH for 50 hours. After heat treatment, specimens were irradiated for 50 hours again.

Colour measurement

The colour of the surface of specimens was measured with a colorimeter (SE-2000: Nippon Denshoku Industries Co., Ltd., Tokyo). The sensor head was 6 mm in diameter. Measurements were made using D₆₅ illuminant and a 2° standard observer. The tristimulus value X, Y, and Z of all specimens were obtained from the colorimeter. 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.

$$\Delta L^* = L^*_t - L^*_c \quad (1)$$

$$\Delta a^* = a^*_t - a^*_c \quad (2)$$

$$\Delta b^* = b^*_t - b^*_c \quad (3)$$

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

RESULTS AND DISCUSSION

Acetylation before photo-thermal treatment

Figure 1 shows the changes in colour of Japanese cypress by treatments. The ΔL^* of unacetylated wood decreased with light-irradiation, and remarkably decreased by heat treatment after exposure to light. When the specimens were exposed to light again, it increased. The Δa^* increased slightly by light-irradiation and increased sharply by heat treatment. After heat treatment, Δa^* decreased with light-irradiation. The Δb^* increased with light-irradiation, followed by decreasing during heat treatment and increased again slightly by the second exposure to light. The changes in colour by the treatment of process up to heat treatment concur with previous results (Mitsui *et al.* 2001, Mitsui 2004). The change in colour resulting from light-irradiation after heat treatment (*i.e.* the second light-irradiation) shows that the photo-thermally treated wood discolours by exposure to light.

On the other hand, little change in ΔL^* and Δb^* was observed with acetylation, and only Δa^* decreased slightly. With acetylated wood, the ΔL^* changed to the positive, the Δa^* decreased, and Δb^* increased by light-irradiation. This results shows that acetylation is effective to

reduce the colour changes by light, compared with unacetylated wood, as many researchers mentioned (Feist *et al.* 1991, Plackett *et al.* 1992, Ota *et al.* 1996, 1997, Ohkoshi 2002). However, heat treatment after light-irradiation (*i.e.* photo-thermal treatment) made the change in colour of acetylated wood greater, and its colour was almost same as the unacetylated one heated after exposure to light. Furthermore, the colour of acetylated wood changed remarkably by light-irradiation after photo-thermal treatment. The degree of its change in colour was more pronounced than that of the unacetylated one, and the acetylated wood discoloured greater than the unacetylated one. The changes in beech were similar to those in Japanese cypress. These results show that the colour of acetylated wood is not stable when it is exposed under special condition, that is, heat treatment after light-irradiation. Moreover, the colour of the acetylated wood browned by the photo-thermal treatment is more changeable than that of unacetylated one by exposure to light.

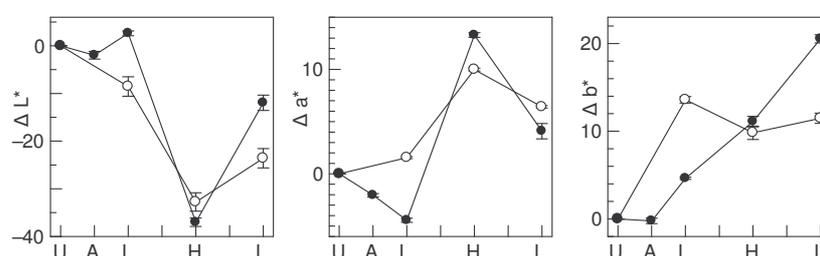


Figure 1: Changes in colour of acetylated Japanese cypress by photo-thermal treatment. U: untreated, A: acetylation, L: light-irradiation, H: heat treatment.

Acetylation after photo-thermal treatment

Figure 2 shows the effect of acetylation on the changes in colour of photo-thermally treated Japanese cypress. The ΔL^* and the Δb^* of photo-thermally treated cypress increased by acetylation. On the other hand, the Δa^* hardly changed. However, the light-irradiation after acetylation made ΔL^* increase greater and Δa^* decrease. The changes in colour of beech were similar to those of Japanese cypress. These results show that acetylation is unsuitable for colour stabilisation of wood coloured by photo-thermal treatment against light-irradiation.

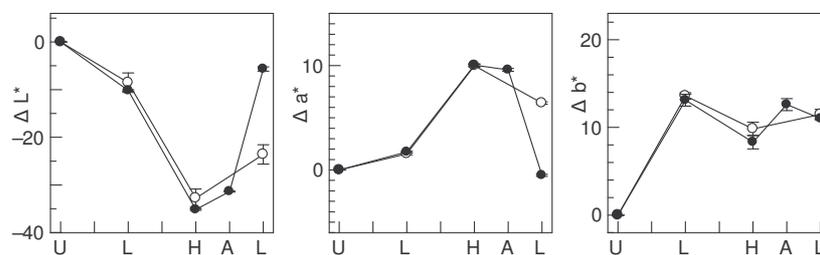


Figure 2: Effect of acetylation on the change in colour of photo-thermally treated Japanese cypress. U: untreated, A: acetylation, L: light irradiation, H: heat treatment.

In a future study, we will examine the changes in the chemical components using IR and NIR spectroscopy, and discuss suitable methods for colour stabilisation of photo-thermally treated wood.

CONCLUSIONS

We discussed the changes in colour of acetylated wood by photo-thermal treatment and the application of acetylation to photo-thermally treated wood. Acetylation made the colour stabilisation of untreated wood against exposure to light increase. However, the colour of acetylated wood changed as great as that of unacetylated one by photo-thermal treatment. Moreover, light-irradiation after photo-thermal treatment made the wood discolour. Also, the wood acetylated after photo-thermal treatment discoloured by light-irradiation. Therefore, acetylation is unsuitable for colour stabilization of wood coloured by photo-thermal treatment against light-irradiation.

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CHAPTER 3

RESINS AND WAXES

UPSCALING AND PROCESS DEVELOPMENT FOR WOOD MODIFICATION WITH N-METHYLOL COMPOUNDS USING SUPERHEATED STEAM

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Keywords: DMDHEU, dimethyloldihydroxyethylenurea, upscaling, superheated steam, process development

ABSTRACT

For nearly twenty years, investigations have been done in order to modify wood using N-methylol compounds (Nicholas and Williams 1987) especially with the well-known DMDHEU (dimethylol-dihydroxyethylenurea). A series of publications show improved properties of small wood samples treated with these textile resins (Militz 1993, van der Zee *et al.* 1998). Most notably, the durability against fungal attack and the dimensional stability can be increased. The modification is based on impregnation of the wood with the formulation in a vacuum-pressure treatment, followed by a curing step at temperatures above 100°C. Using small wood blocks, the treatment appears to be unproblematic, but with bigger dimensions, problems like non-uniform distribution of reactants, crack initiation and discoloration of wood pieces may occur. In our work, a method has been developed which allows for the modification of wood in large dimensions on an industrial scale. It is shown that the selection of different process conditions affects the quality of the treated wood markedly. Choosing the appropriate conditions, the target property profile of the modification (enhanced durability, improved swelling and shrinking behaviour and increased hardness) can be obtained, while avoiding negative impacts on the wood. Some properties are strongly linked to the changing curing conditions, like the enhancement of durability against fungal attack and the release of formaldehyde, while other characteristics like chemical distribution are more or less independent of process parameters. The work provides the basis for the optimisation of the curing process to produce tailor-made properties of the modified wood for different uses.

INTRODUCTION

Wood is a three-dimensional composite made up predominantly of cellulose, hemicellulose and lignin. These polymers are the main building blocks of the cell wall responsible for the physical and chemical properties but are also responsible for the disadvantages of wood (Rowell 1983). Chemical wood modification is an adequate strategy to improve the critical wood properties like durability, or dimensional stability.

Many investigations done in the last two decades show a very good potential for enhancing biological resistance and reducing swelling and shrinking of wood by the use of DMDHEU with small wood blocks (Nicholas and Williams 1987, Videlov 1989). For wood in bigger dimensions, problems like unequal distribution of agent or especially crack initiation during the curing step may occur. Furthermore, deformations and discoloration can be observed and the influence of wood modification on other wood properties is unknown.

The challenge is to develop an ideal process combining optimised curing and drying conditions, which allows the use of the technology on an industrial scale. Temperatures above 100°C are needed for the reaction of DMDHEU without inducing the well known curing and drying failures mentioned before.

The targets of this investigation are:

- Development of a high temperature process for the chemical wood modification with DMDHEU suitable for industrial scale
- Investigation of the influence of different curing conditions on the enhanced properties of modified wood
- Determination of the dependency of drying quality on curing process conditions

EXPERIMENTAL

Materials

DMDHEU and catalyst

As reactive agent, a formulation based on modified dimethyloldihydroxyethylenurea (mDMDHEU) was used. Magnesium chloride was added as catalyst in a concentration of 1.5 % related to the total solution quantity.

Wood

Mixed pine sapwood and pine heartwood (*Pinus sylvestris*, L.) samples with the dimensions 1400 x 100 x 35 mm³ were used. For each curing process, between 130 and 150 replicates were used. As under more practical conditions, the wood quality and orientation of the year rings were very unequal. High quality panels without knots, resin or other failures as well as panels with a lot of failures were used. After curing of these panels, the drying quality was evaluated and boards were chosen schematically and cut into smaller failure free pieces for the following investigations. As controls, non-modified samples with the same quality were used.

Methods

Treatment

The pine boards were vacuum pressure impregnated (1 h, -0.94 bar; 2 h, +12 bar) and the solution uptake was determined. Afterwards, the samples were placed in a drying kiln designed for drying with superheated steam. Six different curing processes were evaluated and with each process two settings have been used, in order to test the reproducibility of the process. Key parameters for the various drying phases of the different processes are:

- Wet-bulb temperature
- Dry-bulb temperature
- Relative air humidity
- Treatment time

All these parameters can be varied in the heating phases, the combined curing-drying phases and as well in the cooling and the conditioning phases.

Determination of the effect of process conditions on fungi

The determination of the effect of process conditions on wood attacking fungi was carried out according to European Standard EN 113. The specimens (ten replicates for each process) were cut out of pure pine sapwood boards with an average solution uptake of approximately 140 % related to the absolute dry wood mass. All samples were leached according to European Standard EN 84 and afterwards dried for 24 hours at 103°C. The untreated control samples were not leached but only dried before testing. The following fungi were used: *Coniophora puteana* and *Gloeophyllum trabeum*.

Influence of process conditions on release of formaldehyde

The influence of process conditions on the release of formaldehyde was determined using the flask method according to European Standard EN 717-3. For this purpose, approximately 20 g of treated wood cut into cubes was stored in polyethylene bottles of 500 ml over 50 ml distilled water for 24 hours in a drying chamber at a temperature of 40°C. The cubes were cut out of 9 boards of each process equally distributed in the stack of blanks.

The emitted formaldehyde was absorbed in an aqueous solution and analysed using the acetyl-acetone method. The mean value of four determinations was calculated and related to the dry weight of the treated wood (mg formaldehyde per 100 g dry wood).

Influence of process conditions on drying quality

According to the recommendation of the European Drying Group (EDG) the different curing charges were evaluated and dedicated to the quality classes 'Standard' (S), 'Quality' (Q) and 'Exclusive' (E) concerning the following criteria:

- Variation of average moisture content ($u_{1/3}$)
- Variation of moisture content differences in single boards ($u_{1/2} - u_{1/6}$)
- Casehardening
- Surface cracks
- Inner cracks
- Discoloration

For most of the mentioned criteria, measurable data and exact limit values are defined in the recommendation. Determination of discoloration is only qualitative. For the classification of a drying or curing batch in the above quality classes, a defined percentage of the boards must meet the requirements.

Effect of process conditions on distribution of DMDHEU

In order to determine the distribution of the reactant depending on the curing process 9 boards per process were chosen. Each board was cut into halves and out of cross sections in the middle and at one end of the

board and in each case four samples of splinters were drilled out (one out of the centre, one out of upper corner, one out of bottom corner, one in between).

The samples were extracted in a 6 percent solution of hydrochloric acid in a water bath at 85°C for 16 h in order to hydrolyse the acetal bonds and dissolve the DMDHEU. The quantification of DMDHEU was carried out indirectly by determination of free and cleavable formaldehyde according to the chromotropic method (Roffael 1982). With the exception of the low formaldehyde content in untreated pine wood, cleavage of DMDHEU is the only possible source of formaldehyde so that this method is suitable for the determination of the amount of reactant.

RESULTS AND DISCUSSION

Results

Resistance against fungal attack

Figure 1 shows the mass loss of the specimens in the fungal test. During the testing period of 16 weeks according to EN 113, *Gloeophyllum trabeum* caused a weight loss of untreated control samples of approximately 40 %. Treated samples of all tested processes showed a strongly increased resistance and minimal mass losses.

Using *Coniophora puteana* as the testing fungus, the weight loss of untreated and treated samples was higher. The differentiation of mass loss and standard deviation of mass loss in relation to different curing processes is possible with this test fungus. The mass loss varies between 4 % (process E) and 20 % (process C).

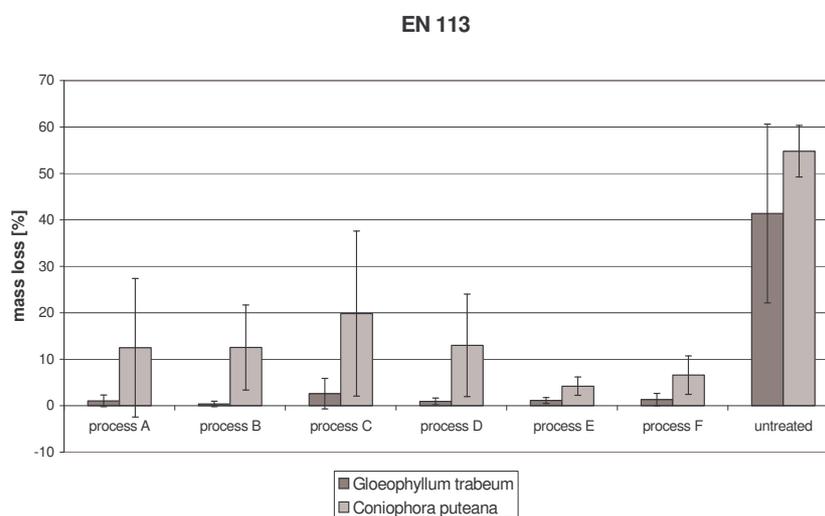


Figure 1: Mass loss of untreated and DMDHEU treated specimens cured at different process conditions in fungal test EN 113 with *Gloeophyllum trabeum* and *Coniophora puteana*

Release of formaldehyde

Figure 2 illustrates that the variation of curing conditions influences the release of free formaldehyde. Cubes made of boards cured in process A caused a more than five times higher concentration of formaldehyde in

the aqueous solution of the implemented bottle test than cubes made of boards cured in process F. Using the same reagent in the same concentration it is possible to reduce the emission of formaldehyde drastically by variation of the conditions in the curing process.

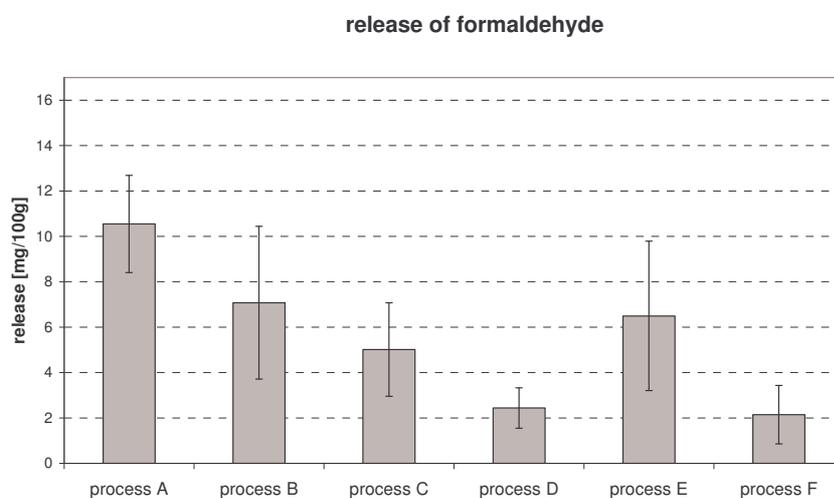


Figure 2: Formaldehyde release of DMDHEU treated specimens cured at different process conditions in flask method according to EN717-3

Table 1: Drying quality of board charges treated with DMDHEU cured in different curing processes determined following EDG Recommendation “Drying Quality”

	Drying quality determined according to EDG Recommendation concerning:					
	Variation of average moisture content ($u_1/3$)	Variation of moisture content differences in single boards ($u_1/6-u_1/2$)	Case-hardening	Surface cracks	Inner cracks	Dis-coloration
Process A	“standard”	“exclusive”	“quality”	marginal	moderate	light uniform
Process B	“quality”	“exclusive”	“quality”	marginal	moderate	light uniform
Process C	“standard”	“quality”	“quality”	marginal	marginal	medium uniform
Process D	“quality”	“quality”	“exclusive”	marginal	severe	severe non-uniform
Process E	“quality”	“exclusive”	“quality”	marginal	moderate	light non-uniform
Process F	“quality”	“exclusive”	“exclusive”	marginal	marginal	severe non-uniform

Drying quality

It is well known for all kinds of drying techniques, that the choice of relevant drying conditions can cause or avoid drying failures. As expected in the above study, the choice of curing process conditions also resulted in different drying qualities of DMDHEU-treated wood. All curing processes produced a similar quality concerning distribution of moisture content. However significant differences in regard to inner cracks and discoloration occurred.

Distribution of DMDHEU

Figure 3 shows examples for all tested processes, indicating that uniform distribution of the modification agent across large size wood

samples is achieved using a superheated steam process. The reagent content in the samples was probed *via* HCl treatment and extraction and determination of total formaldehyde content in the extract.

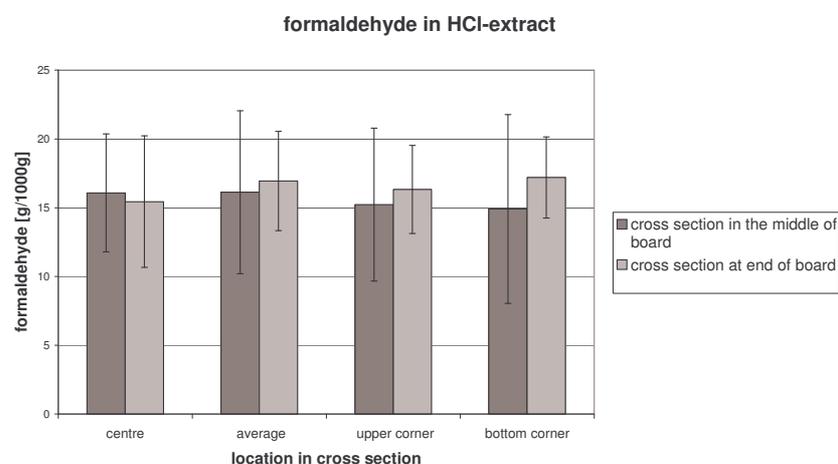


Figure 3: Formaldehyde content in HCl-extract out of differently located samples of process C

Discussion

Resistance against fungal attack

The treatment of pine wood with mDMDHEU led to a complete protection against the attack of *Gloeophyllum trabeum* independent from the chosen conditions of the six tested curing processes. In case of the test fungus *Coniophora puteana* all processes showed an enhanced durability. However, differences related to variations of process parameters were observed. Process E provides wood material with a mass loss of less than 5 %, as required for natural wood species in durability class 1. Other processes, although formulation, concentrations and pre-treatment conditions being constant, different mass loss results were observed.

The finding explains different results with DMDHEU modified wood reported in the literature.

While Videlov (1989) obtained DMDHEU-modified pine with complete protection against *Coniophora puteana*. Militz (1993) reported an insufficient reduction of mass loss using the same reagent with an even higher weight gain of 20 %. Only the curing conditions were different, so that the observed discrepancy of resistance against fungal attack can be clearly explained by the above studies.

Release of formaldehyde

The present experiments show a strong connection between curing conditions and release of formaldehyde from DMDHEU treated wood, measured according to the flask method described in European Standard EN 717-3. It is possible to minimise the formaldehyde emission of the modified wood using optimised processes.

Drying quality

The processes A and B yield the best drying qualities, but in view of other properties of treated wood mentioned above they are suboptimal.

On basis on these results further investigations have to be done in order to find an ideal combination of different process phases for achieving the desired product properties.

Distribution of DMDHEU

Curing of DMDHEU with superheated steam is an adequate method in order to achieve an even distribution of chemical in treated specimens. This is independent from details of process parameters. The high standard deviations of the results depicted in Figure 3 are a consequence from variable penetration during the vacuum pressure impregnation, especially caused by the differences between sapwood and heartwood but also because of knots or clusters of resin.

CONCLUSIONS

The modification of wood with DMDHEU offers significant improvements of key-properties like high resistance against fungal attack and high anti shrink efficiency. In order to realise these properties and to avoid any negative side effects, the careful control of the process parameters is essential.

The above study describes how the modification process can be applied for large scale samples. It provides the basis for the required optimisation of process parameters for producing modified wood with a unique property profile and tailor-made for the desired application. It also shows that the use of superheated steam is suitable for the curing step and allows the production of wood treated with DMDHEU on an industrial scale.

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FUNGAL RESISTANCE, DIMENSIONAL STABILITY AND ACCELERATED WEATHERING PERFORMANCE OF N-METHYLOL TREATED VENEERS OF *FAGUS SYLVATICA*

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Keywords: Beech, DMDHEU, *Fagus sylvatica*, N-methylol, plywood, veneers

ABSTRACT

For wood modification, thin veneer sheets have several advantages compared to solid wood, such as good treatability and lowered internal stresses. Short impregnation cycles and high curing temperatures can be used for the modification process. Sliced beech veneer sheets (*Fagus sylvatica*) were modified with various concentrations of DMDHEU (1,3-dimethylol-4,5-dihydroxyethyleneurea) and mDMDHEU (modified DMDHEU) based formulations. The treatment process consists of three steps, including vacuum impregnation, pre-drying and polycondensation of the chemical in a hot press. After treatment, the veneers show a weight gain of up to 44 % depending on the concentration of the impregnation solution. The chemical agents cause high cell wall bulking and ASE (anti shrink efficiency) of up to 75 %. The treated material is resistant against *Trametes versicolor* and *Coniophora puteana*. After 8 weeks of decay, some of modified veneers showed mass losses as low as 3 %. For accelerated weathering, five layer plywood made of treated veneer sheets was produced. A hot melting phenol formaldehyde resin was used for gluing the material. Some samples were coated with clear coat and water based scumble. The plywood samples were weathered and evaluated according to the EN 927-6. After testing, the modified plywood showed high form stability and good surface qualities. Furthermore, the performance of coating systems applied on modified plywood was improved.

INTRODUCTION

In consequence of the reorganisation of the German forestry, the natural wood growing sequences will be amplified. In the most middle European locations with a temperate Atlantic climate, *Fagus sylvatica* would be the main part of the climax forest. This will lead to an increased availability of beech within the next decades. Although beech experienced a large demand from the Chinese market from 1999 to 2002, the area of application is limited. This is mainly caused by its low bioresistance and dimensional stability. According to the EN 350-2 it is classified in durability class 5, and in treatability class 1.

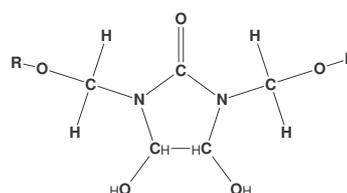
In Germany, beech is the most used wood species in the veneer industry, but its market share decreased from 44.4 % to 23.7 % within the last three years (VDF 2002, VDF 2004). The reason for this is the present trend towards dark coloured wood species in the furniture industry. Right now, beech is limited for decorative and constructive indoor applications. Against the background of the good treatability, the increasing availability and the limited application range beech is predestined for use in chemical wood modification. Different authors have already investigated solid beech wood dimensions in combination with different resin treatments, acetylation with acetic anhydride and

furfurylation (Militz 1991, Militz 1993, Westin *et al.* 2003). Depending on the modification technique, the resistance against fungal attack as well as the dimensional stability have been improved. Acetylation and resin treatment with N-methylol compounds can cause an ASE (=Anti Shrink Efficiency) of more than 60 % under lab scale conditions. In the same way, the resistance against wood decaying basidiomycetes, like *Trametes versicolor* and *Gloeophyllum trabeum*, can be improved (Militz 1991, Krause *et al.* 2003, Verma 2005). Admittedly, modification of solid wood with water based liquids in industrial scale often shows complex problems, because of internal stresses and a non-uniform discolouration. As a result of the low cross sections, even wood species, which are hardly treatable, like spruce, can be modified in veneer thickness (Wepner 2002). Against this background, treatment processes for veneer modification has advantages compared to solid wood modification.

EXPERIMENTAL

Chemicals

Two formulations based on DMDHEU (1,3-dimethylol-4,5-dihydroxyethyleneurea) and mDMDHEU (modified DMDHEU), provided by BASF AG, were used for modification process (see Fig. 1). As catalyst, a concentration of 5 % $MgCl_2 \cdot 6H_2O$ was added. To achieve different chemical concentrations in the veneer, the formulations were diluted with demineralised water. Thus liquids with 10 % to 50 % of the stock solution were adjusted.



DMDHEU: R = H

mDMDHEU: R = CH₃

Figure 1: Chemical structure of DMDHEU and mDMDHEU

For plywood production, a hot melting phenol formaldehyde resin (Dynea: DYNOSOL S-576) was used. Moreover, the samples were coated with a clear coat based on linseed oil (Clou: Yachtlack) and a water based scumble (Sikkens: Cetol WF 780; RAL No. 009).

Process

The veneer treatment process consists of three steps (see Fig. 2). To guarantee a complete impregnation of the whole cross section, a vacuum of 40 mbar for 30 min followed by 2 h storing at atmospheric pressure in the solution was used. By a drying step the excessive water was removed afterwards. Therefore, the veneers were stored in a drying kiln with a permanent air flow at 120°C, until a wood moisture content below fibre saturation point was reached. During the third process step, the N-methylol compounds were reacted and cured. At a temperature of 140°C and a specific pressure of 2 N/mm², the polycondensation of the chemical took place in a hot press. For the single veneers, a pressing time of 7 min was used. For plywood production the gluing and curing

step was combined. The pressing time has to be extended according to the number of veneer layers.

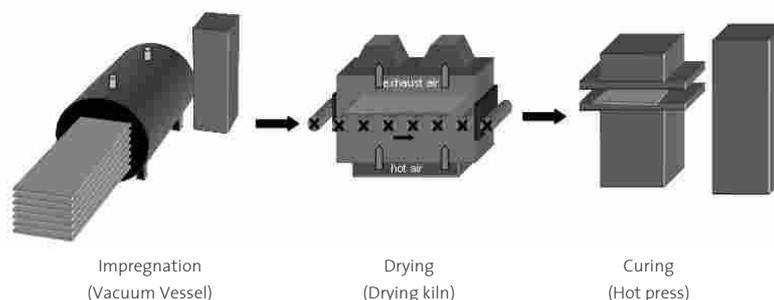


Figure 2: Process steps for N-methylol treatment of beech veneer sheets including 1. Impregnation; 2. Drying; 3. Hot pressing

For further evaluation, the veneers were oven-dried at 103°C for 24h and the Weight Percent Gain (WPG) as well as the bulking effect was calculated (Eqns. 1 and 2).

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

$$\text{Bulking (\%)} = ((L_1 - L_o) / L_o) \times 100 \quad (2)$$

Where: WPG = weight percent gain; m_o = mass of untreated oven-dry sample; m_1 = mass of modified oven-dry sample; L_o = radial length of untreated oven-dry sample; L_1 = radial length of modified oven-dry sample.

Wood material

The wood material used for the investigations were beech veneers (*Fagus sylvatica*). The bioresistance and the sorption behaviour were investigated with sliced veneers with a thickness of 0.5 mm. For plywood production rotary peeled veneers with a thickness of 1.5 mm were used.

Sorption behaviour

The sorption behaviour was investigated with veneers of 50 x 50 x 0,5mm³. They were climatized at relative humidities (RH) of 30 %, 50 %, 65 %, 83 %, 90 % and 95 %. The maximum swelling was determined after water impregnation at a vacuum of 40 mbar followed by 2 h storing at atmospheric pressure. After each climatization step, the weight and radial dimension was measured. Equilibrium Moisture Content (EMC), radial swelling and ASE was determined according to the following equations (Eqns. 3, 4, 5).

$$\text{EMC (\%)} = ((m_2 - m_1) / m_1) \times 100 \quad (3)$$

$$\text{S(rad) (\%)} = ((L_2 - L_1) / L_1) \times 100 \quad (4)$$

$$\text{ASE(rad) (\%)} = ((S_2 - S_1) / S_1) \times 100 \quad (5)$$

Where: EMC = equilibrium moisture content; m_1 = mass of oven-dry sample; m_2 = mass of modified climatized sample; S(rad) = radial swelling of the sample at a specific climate; L_1 = radial length of the oven-dry sample; L_2 = radial length of the climatized sample; ASE(rad) = anti shrink efficiency in radial direction

S_1 = radial swelling of untreated sample at water saturation; S_2 = radial swelling of modified sample at water saturation.

Fungal Resistance

The resistance against the white rot fungus *Trametes versicolor* and the brown rot fungus *Coniophora puteana*, was determined with veneer samples of 40 x 40 x 0.5 mm³, according to a modified EN 113 procedure. To facilitate the removal of mycelia after decay, the samples were wrapped in stainless-steel wire netting of 100 x 30 x 1 mm³ with a mesh size of 1 x 1 mm². After sterilisation with gamma radiation, two treated and two untreated samples were placed into petri dishes for 8 weeks. The extent of fungal attack was determined based on weight loss.

Accelerated weathering

For accelerated weathering exposure, specimens of interlace treated and untreated beech plywood boards with five layers of 75 x 150 x 7.5mm² were prepared. The test cycles in the QUV-tester were adjusted according to prEN 927-6. One cycle includes 1. step: 24 h condensation (45°C); 2. step: 16 recurrences of step 3 and 4; 3 step: 2h UV light (60°C); 4 step: 1 h sprinkling; 5 step: 24 h condensation (45°C); 6 step: 24 recurrences of step 7 and 8; 8 step: 1 h sprinkling. After each cycle, the samples were classified with respect to discolouration, cracks, deformation and delamination. Therefore five evaluation classes from "0" = unchanged to "5" = completely changed were defined.

RESULTS AND DISCUSSION

Weight gain and bulking effect

The WPG increased linear to the concentration of N-methylol compounds in the impregnation solution (Fig. 3). Comparable results are known from Scots pine (*Pinus sylvestris* L.) in solid wood dimensions (Krause *et al.* 2003). A filter effect, which results in a non-uniform allocation over the whole cross section, as is known from some water soluble wood preservatives (Leithoff 2005), was not observed. The bulking effect behaves the same with both agents, whereas the correlation to the amount of chemical in the veneer is not linear (see Fig. 4).

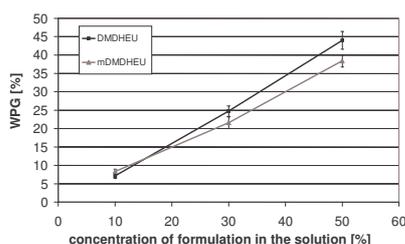


Figure 3: Weight gain of treated veneers related to the concentration of DMDHEU and mDMDHEU in the solution

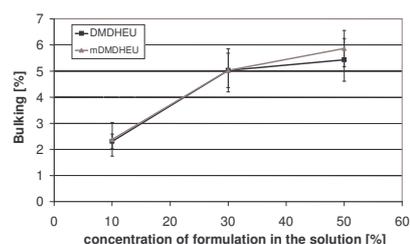


Figure 4: Bulking of treated veneers related to the concentration of DMDHEU and mDMDHEU in the solution

Compared to the maximum radial swelling of untreated veneers of approximately 7.5 %, a bulking effect of 2.5-5.8 % subject to the WPG is high (see Fig. 5-7). Furthermore, a consistent allocation of the agent can be assumed over the whole cross section, because the bulking effect can be defined as amplitude for cell wall penetration.

Sorption behaviour

The dimensional stability and the sorption behaviour of the modified veneers are influenced by the amount and the type of N-methylol compound. An increasing amount in the veneer reduces the radial swelling. This effect is observed over the whole air humidity range (see Figs. 5 and 6). A radial ASE of up to 75 % (mDMDHEU) and 53 % (DMDHEU) is reached with a concentration of 50 % of formulation as the impregnation liquid. Militz (1993) reported a volumetric ASE of 50 % for beech, which was treated with different concentrations of DMDHEU. Comparable results are known from Scots pine and Ponderosa pine (*Pinus ponderosa*) treated with DMDHEU derivatives (van der Zee *et al.* 1998, Nicholas and Williams 1987).

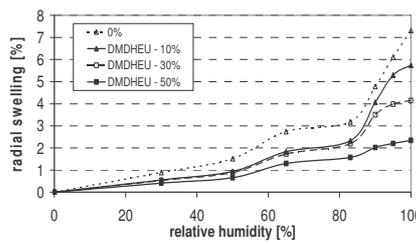


Figure 5: Radial swelling of veneers treated with different concentrations of DMDHEU vs. RH

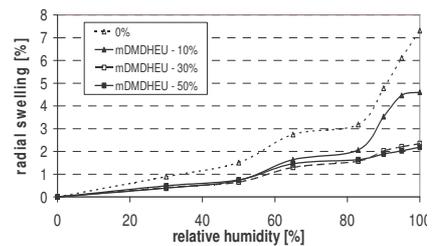


Figure 6: Radial swelling of veneers treated with different concentrations of mDMDHEU vs. RH

After treatment with 30 % mDMDHEU, the hysteresis curve of beech veneers shows a flat gradient (see Fig. 7). The disposition of the bulking effect and the water swelling within one graph clarified that the maximum swelling of the veneers is nearly unchanged. A reduction of the maximum swelling by a cross-linking effect, as is known from Scots pine, was not found (Krause *et al.* 2003).

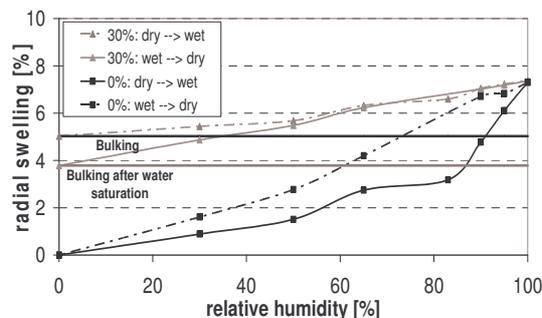


Figure 7: Sorption isotherms of veneers treated with a concentration of 30 % mDMDHEU vs. RH

In relation to the WPG and the kind of chemical, the proportion between the radial swelling and the EMC is changed (Figs. 8 and 9). The untreated samples show a linear correlation between the moisture content and the swelling over the whole air humidity range as is known from literature (Niemz 1993). At 65 % RH and 20 °C the EMC of modified veneers treated with a concentration of 30 % DMDHEU and mDMDHEU is reduced to 7.4 % and 7.0 % compared to an EMC of 11.5 % of untreated samples. By using a chemical concentration of more than 30 % of DMDHEU respective 10 % of mDMDHEU, the EMC increased more than radial swelling compared to untreated veneers at a relative humidity of

more than 65 % and 20°C. Besides, these samples started to feel wet at high relative humidity. This behaviour indicates that the fibre saturation point of modified samples has changed and free water is available in wood structure at relative humidity of less than 100% and 20°C. Presumably, the amount of $MgCl_2$ and of unreacted chemical, both hygroscopic substances, is responsible for this. Krause *et al.* (2003) reported on an increasing EMC by an increasing concentration of DMDHEU and of $MgCl_2$ with Scots pine.

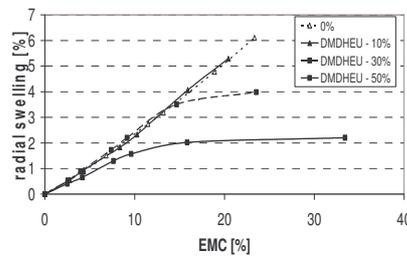


Figure 8: Radial swelling related to the EMC of veneers treated with different concentrations of DMDHEU subjected to the relative humidity of 30%, 50%, 65%, 83%, 90% and 95%

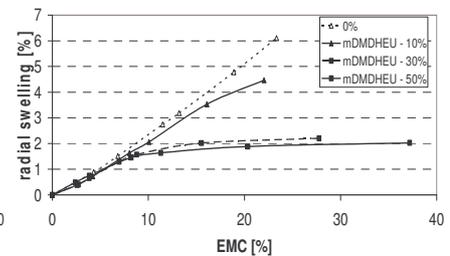


Figure 9: Radial swelling of veneers treated with different concentrations of mDMDHEU subjected to the relative humidity of 30%, 50%, 65%, 83%, 90% and 95%

Resistance to fungal attack

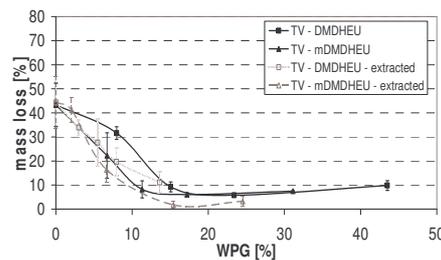


Figure 10: Mass loss of veneers treated with different concentrations of DMDHEU and mDMDHEU after 8 weeks of incubation with *Trametes versicolor*

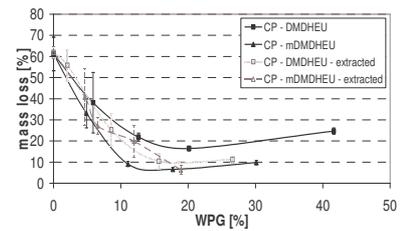


Figure 11: Mass loss of veneers treated with different concentrations of DMDHEU and mDMDHEU after 8 weeks of incubation with *Coniophora puteana*

Before the fungal tests, one part of the samples was extracted in Soxhlet equipment with demineralised water for 8 h, in order to extract unfixed chemicals out of the wood structure. The untreated veneer samples for virulence test of *Trametes versicolor* and *Coniophora puteana* show a sufficient mass loss according to the requirements of EN113. A rise of the chemical in wood causes a reduced mass loss after decay (see Figs. 10 and 11). At approximately 15-20 % WPG the optimum resistance against fungal attack is reached. The unextracted samples show higher mass losses with the same weight gain as the extracted ones. Possibly the high moisture content of more than 100 % during the fungal attack caused a leaching of unfixed chemical. The increasing mass loss of veneers with a WPG of more than 30 % could be explained in the same way. In comparison to *Trametes versicolor* with a minimum mass loss of 1.6 % (15.5 % WPG mDMDHEU), *Coniophora puteana* delivers higher degradation rates of 6.2 % (18.9 % WPG mDMDHEU). Investigations about the resistance of DMDHEU treated mini blocks of

beech showed mass losses below 5 % at WPG higher than 7.8 % (Verma *et al.* 2005). Both samples with a high and samples with a low mass loss after decay were completely overgrown by the mycelia. At the same WPG, the veneers treated with mDMDHEU show a slightly lower mass loss compared with the ones treated with DMDHEU. Until now, the mechanisms of improved resistance are not clarified, although Verma *et al.* (2005) established that these effects are not related to a biocidal effect of DMDHEU.

Accelerated weathering

The occurrence of cracks and the form stability of N-methylol treated plywood is significant is much improved compared to untreated veneers (see Tab. 1). Untreated and uncoated beech plywood samples already failed after the first weathering cycle. Even the highly resistant phenolic glue showed delamination on one untreated sample. After three cycles of accelerated weathering, the surface of untreated and modified plywood samples became lighter.

Table 1: Classification of plywood boards after 3 cycles of accelerated weathering in the QUV-tester

chemical	conc.	coating	delamination	cracks	Discolour-ation	deformation	coating
-	-	-	2.0	2.7	3.0	3.3	-
-	-	clear	0.0	2.3	3.0	1.3	5.0
-	-	scumble	0.0	2.0	3.0	1.0	3.0
DMDHEU	20%	-	0.0	0.0	2.7	0.0	-
DMDHEU	30%	-	0.0	0.0	2.7	0.0	-
DMDHEU	30%	clear	0.0	0.0	3.0	0.0	1.7
DMDHEU	50%	-	0.0	0.0	3.3	0.0	-
mDMDHEU	20%	-	0.0	0.0	2.3	0.0	-
mDMDHEU	30%	-	0.0	0.0	2.3	0.0	-
mDMDHEU	30%	clear	0.0	0.0	2.3	0.0	1.3
mDMDHEU	30%	scumble	0.0	0.0	0.7	0.0	0.7
mDMDHEU	50%	-	0.0	0.0	2.7	0.0	-

This variation is caused by lignin degradation by UV-light and washing out during the sprinkling phase (Fig. 12). The dark colour under the UV-exposed part of the clear coated samples indicates lignin degradation as well. Because the colour change of modified plywood is comparable to untreated wood, the treatment seems to have no influence on the light stability of lignin. Admittedly the washing out effect of the degradation products seems to be slowed down, because of the minor surface roughness of modified samples after decay.



Figure 12: Surface quality after 3 cycles of accelerated weathering in the QUV-tester

Imamura (1991) and Evans *et al.* (2000) reported about such effects with acetylated wood. But, the amount of DMDHEU content in very thin veneers decreased during accelerated weathering in QUV (Xie *et al.* 2005). Due to the improved dimensional and form stability of N-methylol treated plywood, the durability of the clear coat and the scumble system is extended (Fig. 10).

CONCLUSIONS

As a result of the modification of beech veneers with DMDHEU and mDMDHEU the resistance against basidiomycetes, dimensional stability and the performance during accelerated weathering is highly improved. All properties are related to the amount of N-methylol compounds in wood, whereby the optimum against fungal resistance and dimensional stability is reached at a WPG of 15-20 %. The differences in material performance between different formulations are low. The reduced swelling of veneers over the whole air humidity range, which is caused by the bulking effect in the cell wall structure, is responsible for a good form stability and crack performance during the weathering test. Lignin degradation by UV-light cannot be inhibited, whereby the low surface roughness indicates decreased erosion compared to untreated samples. The durability of the coating systems was highly improved.

The present study shows that plywood made of N-methylol modified beech veneers shows considerably better performance against changing climates than untreated samples. Against this background the use of modified beech veneers in hazard class 3 according to the EN350-2 appears to be feasible.

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Opportunities and Limits of Wood Improvement by Surface Treatment with Reactive Resins

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Keywords: ASE, cracks, dimensional stabilisation, synthetic reactive resins, outdoor exposure

ABSTRACT

This research looked at the possibilities of using simple treatment procedures and commercial type reactive resins to improve the dimensional stability of beech wood. The wood samples were treated by immersion in low viscosity solutions of reactive resins and further conditioned at room temperature in order to obtain a thin, inner, waterproof layer of cross-linked resin. This treatment was meant to be just a starting point in a more complex treating scheme including bio-protection and coating and was performed to ensure a better behaviour of wood in outdoor conditions, mainly by limiting water absorption and wood cracking. Research was carried out in three stages: experiments on resins looking at the water resistance of cross-linked resin films, laboratory experiments on treated beech samples for the determination of the water absorption and ASE values and field tests in the conditions of the biological hazard class 3. The evaluation of the field test samples looked especially at the influence of the surface impregnation with reactive resins on the cracking, general aspect changes and biological degradation of coated and uncoated beech samples. The paper presents some experimental results and correlations between the properties of the resin films and the behaviour of treated wood in laboratory water immersion tests and HC 3 field tests. The surface treatment with reactive resins evidently reduced wood cracking in outdoor exposure. The further bio-protection and coating of resin treated wood greatly improved its behaviour in field tests, indicating that despite its principle limits, surface pre-treatment with reactive resins may be considered for some applications.

INTRODUCTION

Wood improvement has been a continuous challenge for researchers around the world and new goals are set up nowadays in the context of the sustainability concept. Extensive research has looked at methods of reducing wood hygroscopicity and improving its dimensional stability (Rowell 1984, Matsuda 1996). Most of the chemical methods employed for this purpose were based on three different principles: chemical modification of wood, wood impregnation with monomers or reactive resins and physical insulation of wood surface by finishing and/or treatment with hydrophobic products (Timar 2003). The first two types of methods, based on deep impregnation with either chemical reagents able to react with wood components, or compounds able to form a cured macromolecular compound inside the wood structure blocking water access, are the most efficient and predominant in the worldwide research effort in this field. However, their practical application is still limited because they involve specialised equipment and high costs.

That is why wood improvement by “*surface impregnation*” with reactive resins might be a simple alternative to “*deep*” wood impregnation procedures. This non-conventional term is introduced to describe the penetration of resins into the wood structure, just in the cell lumens or in the cell lumen and cell walls, but only into a superficial layer. Due to a further *in situ* cross-linking process, a cured product would result, constituting a thin water resistant layer inside the wood. This layer should act as an inner waterproof envelope, blocking or limiting to some extent water access. A reduction of water adsorption/absorption and consequent wood swelling and shrinking could be expected. Some other effects, such as diminution of cracking and a better biological resistance could be further benefits. Based on this theoretical hypothesis the following objectives were addressed by the present research:

- Characterisation of some resins for their potential quality of wood improvement by surface impregnation;
- Establishment of a possible correlation between the resin properties and the dimensional stability of treated wood;
- Establishment of some possible correlations between the dimensional stability of treated wood and its service performance in outdoor conditions (HC3).

Research methodology

A sequential structure of research organised in three phases was adopted in this study. The first phase consisted of laboratory experiments on some synthetic reactive resins looking at the water resistance of the resulting cross-linked films. The second phase consisted of laboratory experiments on treated beech samples for the determination of the water absorption and ASE values, whilst in the third stage the treated wood was field tested in the conditions of the biological hazard class 3. Schematically the methodology is represented in Figure 1.

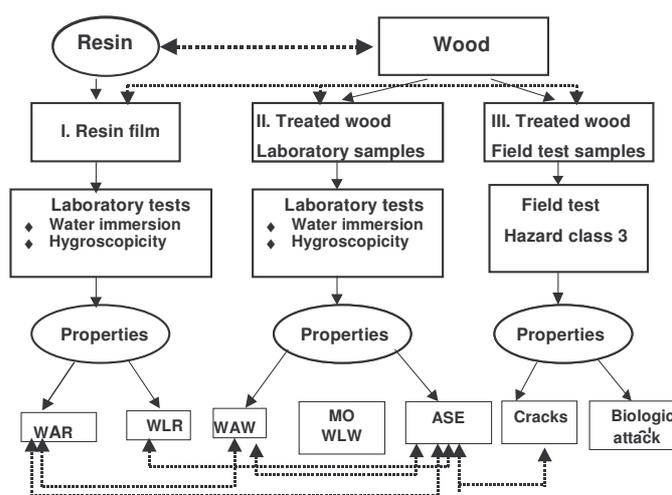


Figure 1: Experimental research phases and possible correlations (dotted lines)

Samples

Glass lamellas of (25 x 40) mm (width x length), initially cleaned and weighed were used as an inert support for resin application. Beech wood (*Fagus sylvatica*) was selected for these experiments using samples with dimensions of 20 x 20 x 30 mm³ in the radial, tangential and longitudinal directions, respectively, prepared for laboratory tests. They were used to determine the dimensional stability of treated wood compared to untreated wood. Measurements on the radial and tangential directions were made on 5 pre-marked points for each test sample. Samples with a triangular profile (of 40 mm sides) and 200 mm length, having two radial faces and one tangential face were used for field tests in the conditions of hazard class number 3 (Sandberg 1999). The wood samples used in these experiments were planed on all surfaces, without defects, such as knots or abnormal coloration. Before treatment, the samples were sanded with abrasive paper H100. All the samples were conditioned in a laboratory conditioning box at 20 ± 2°C and 55 ± 5% RH, until the equilibrium moisture content, of about 9 %, was reached. The laboratory and field test samples used for each phase of the experiments are presented in Figure 2.

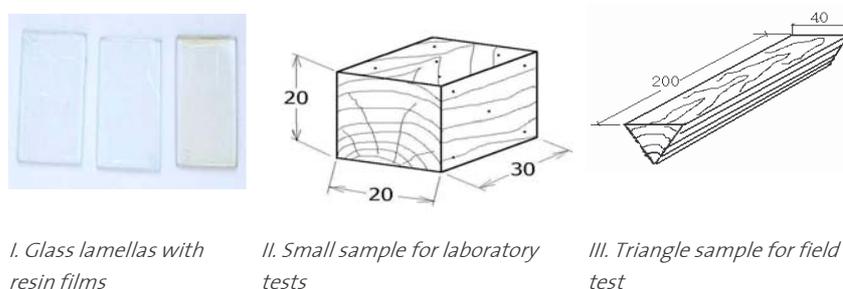


Figure 2: Samples used in the different experimental stages

Treatments

Three types of commercial products based on reactive resins were used in the dimensional stabilisation experiments: an ecological acrylic-polyurethane lacquer (LE), an epoxy resin Epikote 1001 (RE), an alkyd-polyurethane lacquer (LA-PUR). These products were diluted for application to the same low viscosity corresponding to a flow time $T_{sc}=12$ s, $\Phi 4$ mm, 20°C. The types, codes, physical and chemical characteristics of these products as well as the codes of treatments are presented in Table 1.

Table 1: Types of chemical products and codes of treatments

Type of product		Code of resin	Aspect	Solid content [%]	$T_{sc}\Phi 4$ mm, 20°C [s]	Code of treatment	Uptake [g/m ²] (wood)
Reactive resins	Ecological acrylic-polyurethane lacquer	LE	Aqueous opalescent, white solution	24.1	12	Ta-A1	575
	Epoxy resin Epikote 1001	RE	Transparent colourless solution	43.05	12	Tb-A1	267
	Alkyd-polyurethane lacquer	LA-PUR	Transparent, yellowish-brown liquid	28.22	12	Tc-A1	249

The resins were applied on the glass support in six layers to ensure a sufficient final film thickness (50-100 µm) in order to reduce experimental errors. Drying periods of 24 hours were allowed between the successive resin layers. For dimensional stabilisation, the beech

samples were immersed for 15 minutes at 20°C in the resin solutions. Before and after each treatment the samples were weighed in order to calculate the product uptake in g/m² and conditioned at 20 ± 2°C and 55 ± 5 % RH until constant weight.

Testing and evaluation

The laboratory methodology for evaluating the potential wood improvement properties of the resins consisted of repeated immersion tests (three cycles of conditioning at 20 ± 2°C and 55 ± 5 % RH; followed by immersion for 24h at 20 ± 2°C) and a hygroscopicity test at 20 ± 2°C and 98-100 % RH. The water absorption/adsorption of the resin films (WAR, %) and the weight loss of the resin films (WLR, %) related to water solubility were calculated. A similar laboratory test method, consisting of three repeated cycles of conditioning - water immersion of 72 hours/ 20°C, was used for the small treated and untreated wood samples, in order to determine the water absorption in wood (WAW), the swelling coefficients on the R and T directions and the anti-swelling efficiency (ASE).

After treatment and conditioning, the samples for field testing were cut into two parts: one third of each sample was kept in dark conditions as a reference, and the other part was exposed outdoors, above ground, on a special rack at a 45° slope and South-East orientation. Before outdoor exposure, the transverse faces were sealed with water with a resistant epoxy resin. One of the radial faces and the tangential face were exposed simultaneously.

The field test included untreated control samples (M), coated unmodified sample (M-S2), resin treated samples (Ta-A1, Tb-A1, Tc-A1) and also samples which were further treated with a biocide product (Ta-B1, Tb-B1, Tc-B1) and samples that were resin impregnated, treated with biocide and then coated with a white alkyd paint (Ta-B3, Tb-B3, Tc-B3). The evaluation of the field test samples was done by direct visual observation and considered general aspect changes, biodegradation (discolouration and decay) which was graded according to prCEN/TS 12037: 2002(E), cracks in wood (marked on a scale from 0 to 4) and degradation of the coating films (if present).

RESULTS AND DISCUSSION

All the tested resins cured at room temperature produced water resistant films. However, the resulting films were characterised by different water absorption and weight loss, due to water solubility following the immersion test. The highest water absorption was registered for the acrylic-polyurethane resin LE, whilst the lowest was determined for the alkyd-polyurethane film LA-PUR. Surface impregnation of beech wood with these resins reduced water absorption in wood (Figure 3, top), this reduction being the highest for the less hydrophilic resin (LA-PUR) and the lowest for the most hydrophilic one (LE). A dimensional stabilisation effect corresponding to ASE values of 30-70 % after the first immersion test resulted following this limited access of water in beech wood (Figure 4). The stabilisation efficiency could be inversely correlated with the water absorption in resin film or the water absorption in wood (Figure 3 middle).

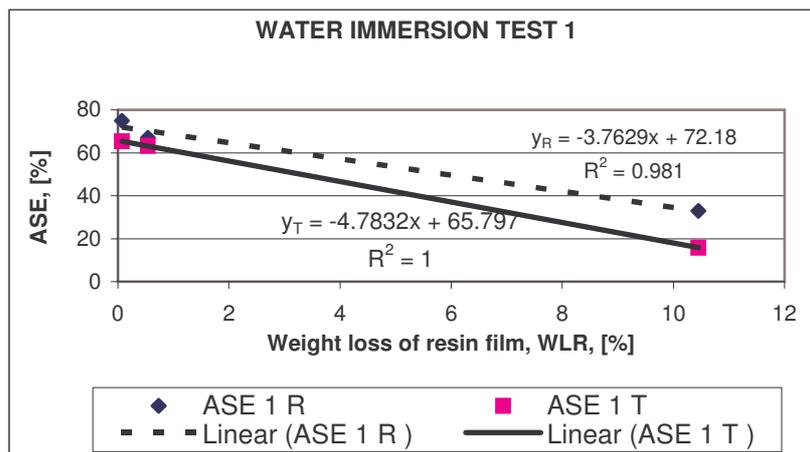
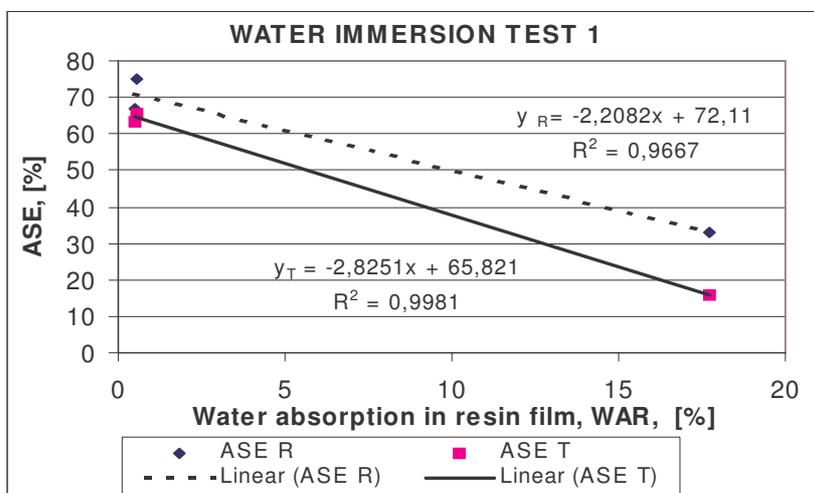
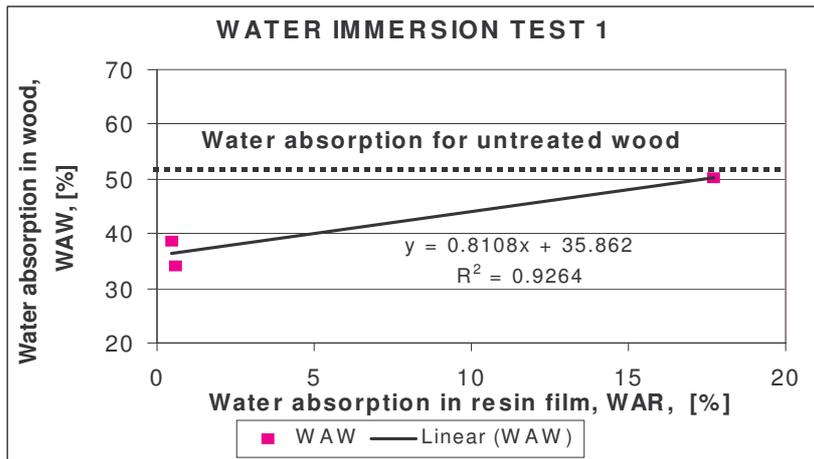


Figure 3: Correlations between water absorption of treated wood and water absorption of resin film (top), ASE and water absorption of resin film (middle), ASE and weight loss of resin film (bottom)

The ASE values after the first immersion test could also be inversely correlated with the weight loss of resin film during the first immersion

test (Figure 3, bottom). These facts could suggest that resins intended to be used for wood improvement by surface impregnation should be characterised by a good water resistance, meaning low water absorption and water solubility after curing, as theoretically presumed. Accordingly, the maximum ASE values were registered for the most water resistant resin film resulting from the alkyd-polyurethane resin (LA-PUR, treatment Tc). However, these improvement effects were not permanent, as shown by the results of the repeated immersion tests. The initial stabilisation effect was drastically reduced and disappeared after the third immersion test (Figure 4).

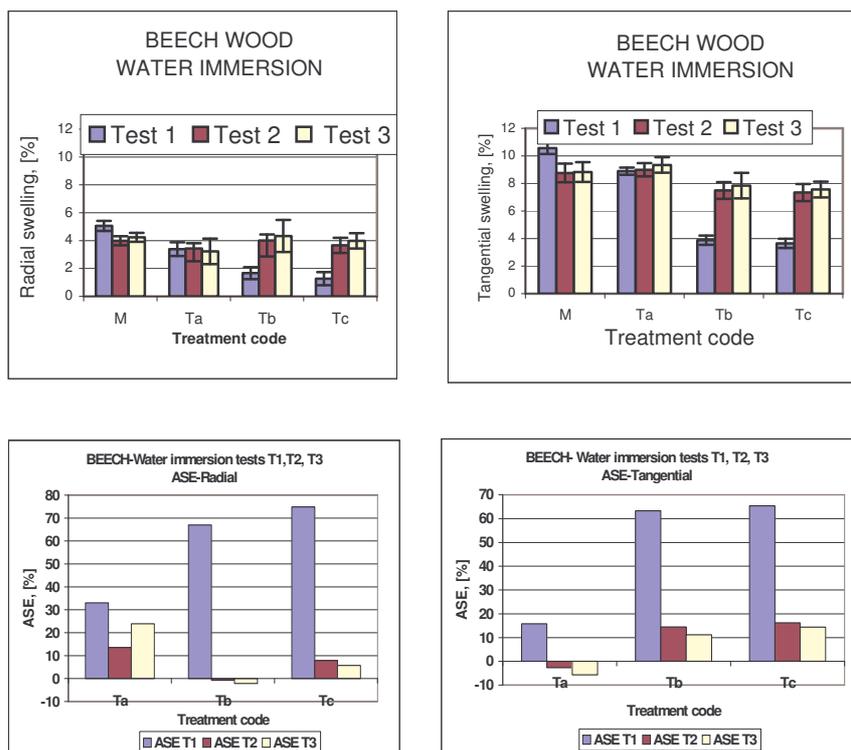


Figure 4: The effect of repeated water immersion on the wood dimensional stabilisation

This fact could only be partially explained as a consequence of resin loss from the treated wood following some cracks in the resin film or delaminating tendencies as suggested from microscopic investigations of treated wooden samples before and after the immersion test. Even fine fissures in wood were detected for some samples for the Tb treatment with the less elastic epoxy resin. Elasticity of the resin films that was not investigated in this research should be very likely an important factor to consider. Even if limited as efficiency and stability, the dimensional stabilisation effect due to surface impregnation with the specified resins had a positive effect on the behaviour of beech wood samples exposed outdoors to the direct action of climatic factors. The treated samples (Ta-A1, Tb-A1, Tc-A1) examined periodically after 2, 8 and 15 months of exposure had less frequent and smaller cracks than the control samples M. The graphs from Figure 6 top, referring to the tangential faces of the triangular samples, indicate that surface impregnation of wood with reactive resins reduced the incidence and intensity of the cracking phenomenon, the positive effect being dependant on the resin type. The intensity of this phenomenon was evaluated by measuring the cumulative length of all the cracks on the tangential face and reporting it to the area of this face.

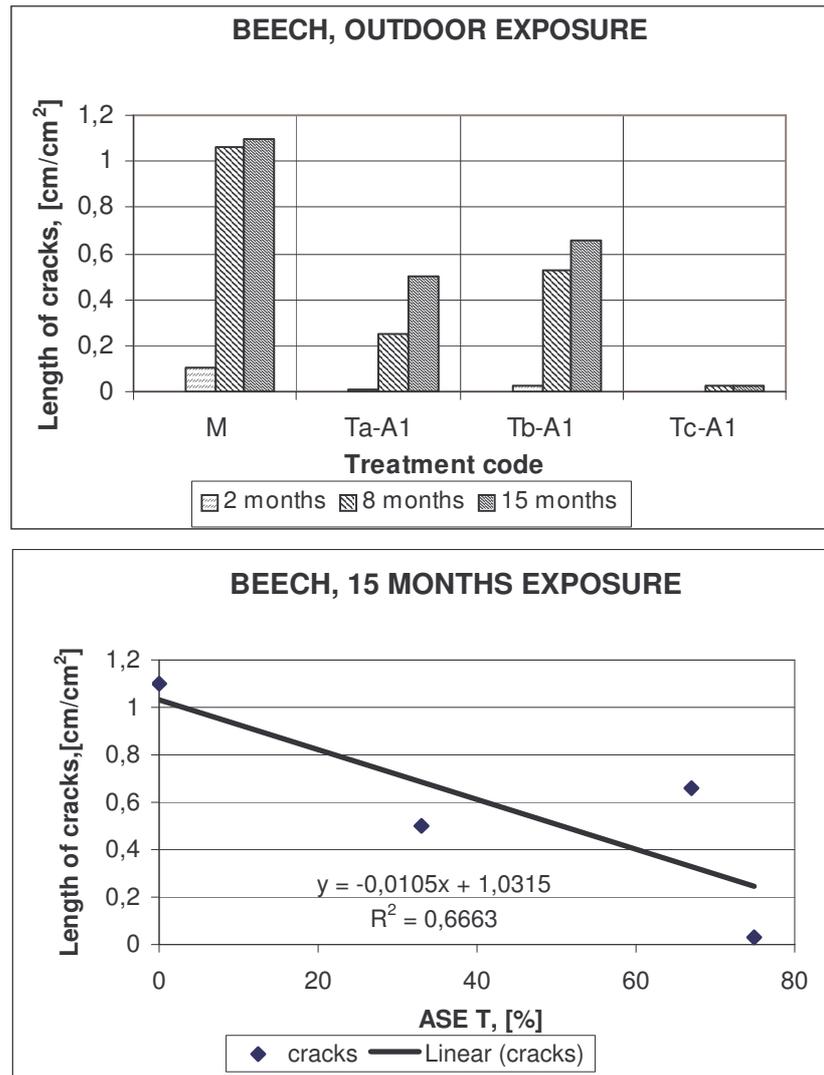


Figure 6. The influence of treatment and exposure period on cracking phenomenon

An inverse mathematical correlation could be established between the intensity of the cracking phenomenon in field test and the ASE values determined in laboratory tests (Figure 6, bottom). It is obvious that more dimensionally stable wood means smaller cracks. However, the confidence parameters of the mathematical equation are not very high and this is caused by the data for the epoxy resin (RE). This was the product with the lowest elasticity of the film that could not withstand swelling and shrinkage stresses. The wood treated with epoxy resin (Tb-A1) had many cracks developed in the resin layer and in the wood. The further bio-protection and coating of resin treated wood greatly improved its behaviour in field tests as suggested by the histograms in Figure 7. This presents comparatively the results from the field test presented in this paper and a modified L-joint test. The results are referring to the intensity of the cracking phenomenon and biological discolouration due to mould fungi, being exemplified for the treatment Tc with alkyd-polyurethane resin.

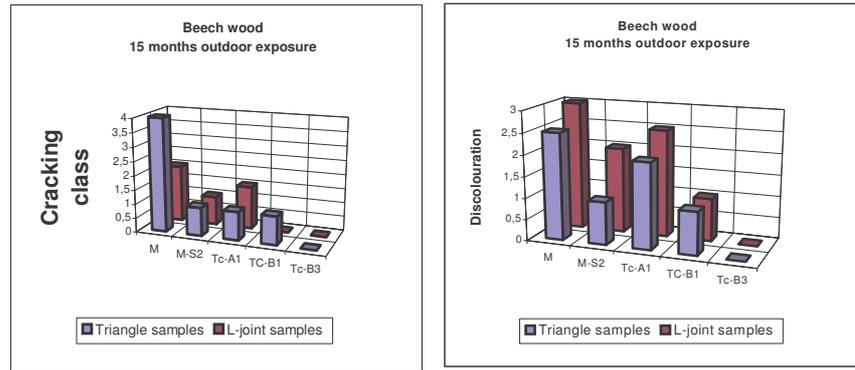


Figure 7: Influence of the surface treatments on the degradation of beech wood after 15 months outdoors, above ground exposure

CONCLUSIONS

The opportunities and limits of a novel and simple wood improvement principle based on "surface impregnation" with reactive resins as a pre-treatment of wood for outdoor applications were investigated. A sequential organisation of the research work was adopted in order to correlate the properties of the resin films with the properties of treated wood and its performance in outdoor exposure in the conditions of hazard class 3. The surface treatment with reactive resins improved its dimensional stability and evidently reduced wood cracking in outdoor exposure. Resin properties, such as water resistance in immersion tests, elasticity and biodegradability influenced the similar properties of treated wood. The further bio-protection and coating of resin treated wood greatly improved its behaviour in field tests, indicating that despite its principle limits, surface pre-treatment with reactive resins may be considered in some applications. The working methodology adopted in this research and the resulted correlations may be a starting point in proposing a useful laboratory method for evaluating the potential efficiency of some other products intended to be used for such wood improvement treatments.

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Process Development of Treatment of Wood with Modified Hot Oil

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Keywords: Oil heat treatment, linseed oil (LSO), rape seed oil (RSO), modified linseed oil (UZA)

ABSTRACT

Joint efforts of industry and research institutes have resulted in the development of an improved thermal treatment with reactive vegetable oils. This work has led to the development and implementation of modified hot-oil for use in the modification of wood at a pilot-scale production stage. In this treatment, the modified oil combines the traditional thermal treatment of wood with chemical modification. Wood with altered properties resulting from both types of treatment is produced by this novel process. Oil heat treatments, using rape seed oil (RSO), linseed oil (LSO) and a modified linseed oil (UZA) were applied to spruce and Scots pine and weight percentage gain (WPG), resistance against fungal attack, colour changes and changes in mechanical properties (MOR and MOE) were examined. The treatment in reactive linseed oil showed superior properties compared to a plain heat treatment (in RSO), except for the changes in colour. The resistances against fungal attack was improved to a high extent, whilst the reduction of the mechanical properties was only minor.

INTRODUCTION

The work in this project has been performed within the framework of a European Craft project called Ecotan (QLK5-CT2002-72467). The project aims to develop a process which can be implemented in practice on a commercially feasible scale and that makes wood more durable by combining reactive oils with thermal modification. The objective is to produce environmentally friendly, high value, durable wood products to compete with high value timber currently imported to the European Union. This will be achieved by using reactive oils derived from natural vegetable oils to protect wood used in targeted high value outdoor applications including gates, cladding, joinery, garden furniture, and high quality fencing. The process research aims to obtain the best results concerning durability of the product, strength of the product, cleanliness of the surface with respect to further processing, aesthetics, and curing of the oils at the surface. All these factors had to be investigated under the condition that the process remains economically feasible. In this paper, results of the first evaluation of material properties and performance of treated material will be presented. Some of the important development steps that have led to the building of a pilot-plant and treatment of wood at pilot plant scale will be described. Different stages and aspects of the treatment process will be elucidated.

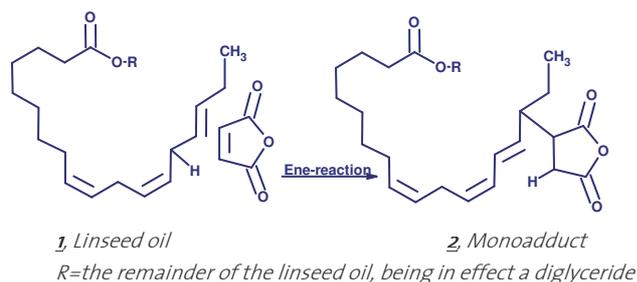
EXPERIMENTAL

Synthesis of the modified (maleinised) linseed oil

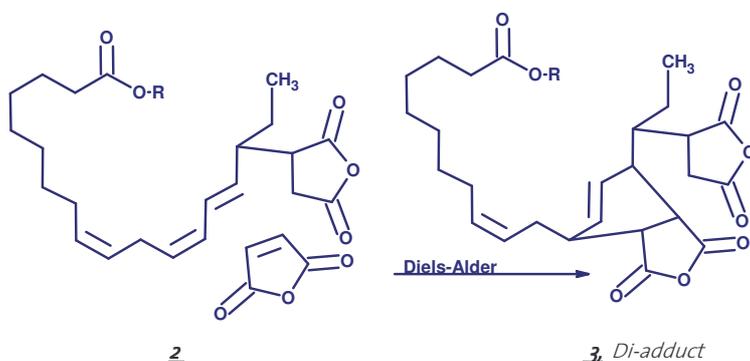
An excellent way of modifying wood in such a way that hydrophobic moieties are attached to the structural elements comprising the wood itself is the use of maleinised fatty acids and their derivatives (Dekker 2002). As the hydroxyl groups in the wood react relatively quickly with the anhydride groups of the resin, the wood modifying agent is rapidly fixed within the wood so that moisture absorption and thus wood rot is prevented.

Preferably the resin is an oxidatively drying resin so that good network formation takes place and as a result a closed film is obtained. The term oxidatively drying resin is well known from alkyd chemistry. Proviso for a good drying ability is not removing all the double bonds when performing the modification. When the ratio of fatty acid to maleic anhydride is kept at or above 1:1 this is automatically taken care of, as is described in a paper by Woo and Evans (1977) which described the process of maleinisation.

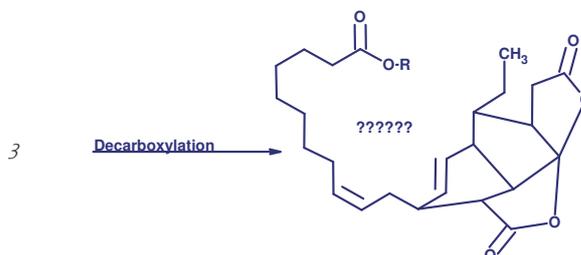
In a first step, maleic anhydride adds to an isolated double bond in the presence of allylic hydrogens, thereby shifting the double bond into isomerisation. This process is known as the “ene-reaction”:



Now that there is conjugation, the system is very susceptible to a Diels Alder cyclo-addition. “Ene”-reactions are known to take place at temperatures above 200°C, whereas Diels-Alder reactions proceed at much lower temperatures, at about 100°C. So, as soon as the first maleic anhydride is added to the fatty acid moiety, the second one proceeds very rapidly:



The di-adduct so obtained is not stable at the temperature of maleinisation. Carbon dioxide is split off via an unknown mechanism. The mechanism postulated by Woo and Evans, yielding a spirodilactone:



seems hardly likely, since the spiro-carbon could not be found in ^{13}C NMR spectra at approx 115 ppm. Nevertheless it should be kept in mind that this decarboxylation occurs and hence the anhydride content can be substantially lower than calculated.

This formation of di-adduct automatically implies that when the fatty acid and maleic anhydride are used in a one to one ratio, this will result in the formation of this di-adduct next to the same amount of unmodified fatty acids. This is very convenient, since we need the unmodified fatty acid for adequate drying properties. In view of its low level of unsaturation, it can hardly be expected that **3** will exhibit proper drying performance.

Process development

For the treatment of wood with the modified linseed oil (UZA) in the process, 4 phases have been distinguished: Impregnation, Dewatering, Heating and Post treatment. The order of the different phases can change and some phases can be merged into one phase. A flow chart of the process is shown in Figure 1

Impregnation

Impregnation always is performed with UZA. With the aim to penetrate the oil into the wood structure, in order to bring the reactive oil in contact with the cell wall material. If the UZA appears to be sensitive for long-term high temperature and/or sensitive for extractives and water from the wood, the impregnation in the first step can be applied under mild conditions (app. 60°C). A pre-impregnation step under mild conditions also will open the opportunity of adding additives to the UZA. Impregnation also can be integrated in the heating phase. During a specified period, pressure can be applied on the oil and wood, after dewatering during the heating up in UZA. Advantage of impregnation during the heating phase is that the viscosity of the oil will be much lower at these high temperatures and the wood structure will be more open for penetration.

Dewatering

In this phase, the water will be evaporated from the wood. This could be done before or after impregnation with UZA. Foam formation of the oil is the biggest problem of this phase. Foaming is the most profound in UZA and less in LSO and even lesser in RSO.

Heating

The heating phase is always after the dewatering. Normally no (extra) pressure is applied during the heating phase. Only when treating in UZA the impregnation is integrated in the heating phase. The standard heating in this set-up has been fixed on 200°C during 3 hours.

Post Treatment

A post treatment can be applied in order to have a better surface cleanness/performance of the wood after treatment. This mainly will be applied when the heating has been performed in UZA. Hot air, LSO or RSO can be used to prevent a sticky surface of UZA on the treated wood. Also vacuum and pressure can be applied to remove residual UZA out of or from the surface of the wood.

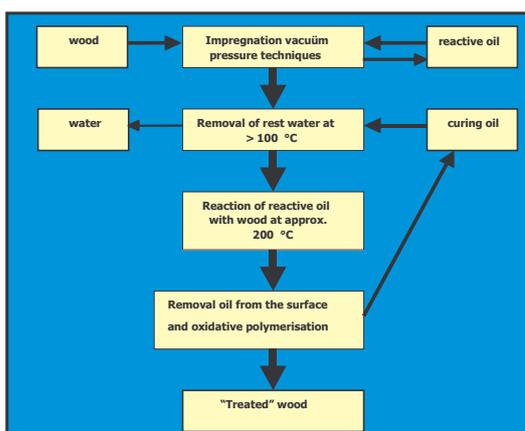


Figure 1: Flow chart of the process

Design of a pilot plant installation

The above-described process has been developed at lab and semi pilot scale at SHR. Foreco Dalfsen in the Netherlands has performed the scaling up to a full operating pilot plant including a 900-litre reactor. A schematic drawing of the pilot plant is shown in figure 2.

The numbers correspond with the following parts of the installation:

- Measure and pressure vessel
- Mirror vessel
- Impregnation and reaction vessel
- Electrical heat exchanger
- Electrical pump
- Storage vessel 1 (oil type 1; UZA)
- Storage vessel 2 (oil type 2; linseed or rape seed, etc.)
- Oil storage

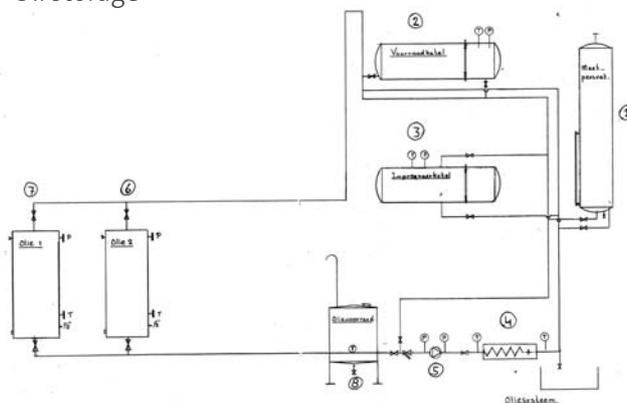


Figure 2: Schematic drawing of the pilot plant



Figure 3: Pictures of the pilot plant; right wood before (top) and after (down) treatment

The storage tanks (6 and 7) are designed with an internal heating system, which allows preheating of the oil. The oil can be circulated in small and bigger loops. When the storage vessels are in the loop these vessels can be used to evaporate the water from the oil. The water has been cooked out of the wood in the impregnation and reaction vessel (3) and transported with the oil to the storage vessels. Vessel 2 can be used for temporary storage of the heated oil, when the reaction vessel is emptied and reloaded with a new batch of wood to be treated. Vessel 1 can be used to put pressure on the reaction vessel. The reaction vessel can additionally be heated by steam, by a jacketed heating system in the double vessel wall. Vacuum can be applied in vessel 1, 2 and 3. Pressure can be applied by both air-pressure and nitrogen pressure.

Evaluation of material properties

The main objective of this study was to gather information about the property changes of wood by application of oil-heat treatments using three different oils. The effect of temperature and the effect of the use of pressure during the treatment-process was examined. Wood samples of different sizes were treated using the MP-2 treatment installation (25 litres) at SHR and changes in durability, MOE/MOR, colour and dimensions as a result of the treatments were analysed.

Material and Methods

Oils

Refined rape seed oil (RSO), refined linseed oil (LSO) and a modified linseed oil (UZA) were used for the wood treatment in the MP-2. In comparison LSO hardens/oxidises faster than UZA but UZA still has good autoxidative properties and can harden without modification or addition of siccatives. RSO is a non-oxidising / hardening oil. The oxidation attitude as well as the viscosity of an oil are of great importance for the cleanliness and/or the quality of the wood surface after the treatment.

Treatment process

The wood (conditioned at 20°C/65 %RH) was placed in a heatable 25 litre reactor vessel. The oils were preheated in an external vessel to approx. 150°C and pumped to reactor vessel. After transfer of the oil, water was cooked out of the wood, using an expansion vessel for picking up water and/or steam from the reactor vessel, while the oil was heated up to 180°C and/or 200°C (*dewatering phase*). After dewatering, applied temperature was kept for in total three hours (*heating phase*). Afterwards the oil was drained to the external vessel and water cooling of the reactor vessel started. At approx. 120°C the reactor vessel was opened and the wood samples were cooled down to room temperature. Table 1 gives an overview of the batches and the treatment parameters.

Table 1: Oils and treatment parameters of the carried out batches in the MP-2

Batch No.	Impregn. oil	Heating Oil	Temp. ³⁾ [°C]
S1	-	RSO	200
S1a	-	RSO	220
S2	-	LSO	200
S3	UZA	UZA	180
S4	UZA	UZA	200
S5	UZA	UZA²⁾	200
S6	-	RSO	220
S7	UZA	RSO	180
S8	UZA	RSO	200
S9	UZA	RSO	220
S10	UZA	LSO	200
S11	UZA	1)	200
S12	UZA	1)	180

1) heating performed in an oven

2) applied pressure during heating 9 bar during 1 hour

3) treatment time on treatment temperature in all batches 3 hours

Tests and test specimens

Specimens of Norway spruce and Scots pine have been treated under the conditions mentioned in table 1. Untreated specimens (for each mentioned size) have been used as a reference. Samples were conditioned before treatment at 20 °C and 65% relative humidity to approx. 12% wood moisture content. The testing methods are described in the following.

Oil retention (Weight percent gain)

The weight percent gain (WPG) caused by uptake of oil during the treatment was determined for all specimen by following equation:

$$\text{WPG} = \frac{m_o - m_1}{m_o} \times 100 \text{ [%]} \quad (1)$$

m_o = mass of the oven dried specimen before treatment

m_1 = mass of the oven dried specimen after treatment

The initial oven dried mass of the specimen was either determined (by oven drying and weighing) or calculated drying reference samples of respective sizes.

Durability testing

The decay resistance against softrot and bacteria was tested in a soil block test according to pr-ENV 807, using standardised "John Innes" soil as medium. The weight loss of the wood samples (5 mm x 10 mm x 100 mm) was measured after periods of , 8, 16, 24 and 36 weeks of soil contact. Beech (*Fagus sylvatica*) and Scotch pine sapwood (*Pinus sylvestris*) were used as reference material. The natural durability of heat-treated and non-treated wood to Basidiomycetes (*Poria placenta* and *Coriolus versicolor*) was tested in an accelerated test based on EN 113. The weight loss of the wood samples (5 mm X 10 mm X 30 mm) was measured after 6 weeks incubation time in the so-called miniblock biotest.

Colorimetric analysis

Changes in colour caused by treatment were examined in two steps. Firstly digital scanings were taken for a visual assessment and secondly a colorimetric analysis was performed. The specimen (150 x 70 x 20 mm) were scanned at three different positions of their

radial (top) surface. The scanner applies a flash on a specific position of the specimens surface and measures the reflected brightness and the wavelength of the reflected light. This data is digitised and expressed as three parameters that give a position in a colour space system, these parameters were L* (indicates lightness), a* and b* (indicating the chromaticity co-ordinates). This L*a*b* colour space is one of the most frequently used methods for measuring object colour.

Strength properties

The MOR and the static MOE was determined after the treatment and compared to untreated samples. Samples were conditioned at 20°C and 65% relative humidity. The measurements were carried out on testing equipment type Zwick 010. The static MOE was determined in a destructive 4-point bending test for specimens with sizes 500 x 20 x 20 mm, according to EN 408 respectively.

RESULTS AND DISCUSSION

Weight Percent Gain (WPG)

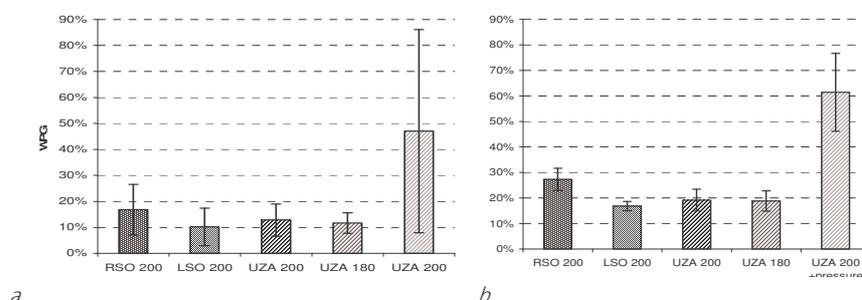


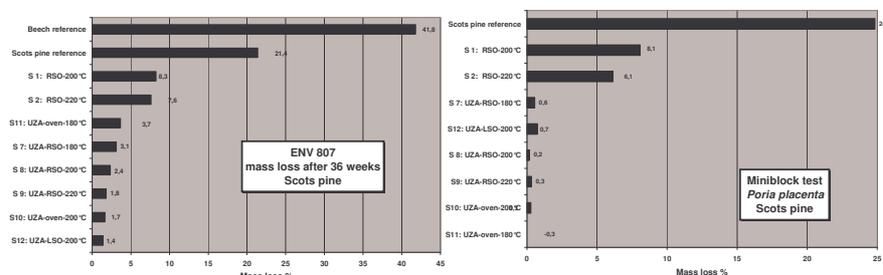
Figure 4: Weight percent gain as a result of the oil-heat treatments. Specimen with dimensions: 500 x 20 x 20 mm (a) and 150 x 70 x 20 mm (b)

Figure 4 shows the WPG caused by the treatment of five applied batches. The results show that application of the oil-heat treatments increases the mass of the specimens, since the extent in which the mass is increased depends on the dimensions and wood species. The WPG derived from both specimen shapes are corresponding, since the values are higher in Fig. 4b (150 x 70 x 20 mm). RSO (16.8 % / 27 %) leads to slightly higher WPG than LSO (10.2 % / 16.9 %) and the UZA applications without pressure UZA 200 (12.8 % / 19.2 %) and UZA 180 (11.7 % / 18.8 %). This may be related to the lower viscosity of the RSO. Furthermore no influence of temperature (UZA 200 / UZA 180) on uptake of oil can be established. With applied pressure (9 bar) during the process (UZA 200 + pressure), WPG gets approx. 2.5 times increased compared to application without pressure (UZA 200). High standard deviations for the batch where pressure is applied (particularly Fig 4a) are caused by the presence of heartwood next to sapwood in the wood samples. Caused by the big differences in oil uptake of the heart wood and sapwood samples, the standard deviations are increasing with applying pressure.

A loss of wood substance that usually occurs with heat treatments (Sailer and Rapp, 2000, Syrjänen and Kangas 2000) could not be observed because of the uptake of oil during the process. The extent in

which wood components have been affected is unknown. According to earlier researches by Buro (1954), Sandermann and Augustin (1963), Kollmann and Fengel (1965) and Sailer *et al.* (2000), it can be suggested that the extent of mass loss is negligible, since under absence of oxygen oxidation reactions are missing.

Durability



Figures: Results of durability testing of treated Scots pine: (L) results miniblock test, (R) results ENV 807 test.

From the results (Fig. 5) it can be seen that the oil treatment improves the resistance against brown rot (R) and softrot (L) to a high extend. This is shown by the low weight losses of the treated samples compared to the untreated reference samples. The same results are found for the white rot testing and for testing of the other treated wood species (a.o. Spruce). Another clear observation is the difference between the (plain) heat treatment in RSO (S1 and S2) compared to the treatment in the reactive linseed oil (UZA). This indicates the extra effect on improving the durability in the reactive oil treatment compared to a "plain" heat treatment. With respect to evaluation of the effect of treatment conditions on the results of the durability, the result of the ENV 807 testing are more suitable since these results are more pronounced. Regarding the results of the ENV 807 a clear temperature effect can be seen, where the 180°C treatments shows minor effects, compared to the higher temperature treatments. More results of the durability testing of this treatment will be published in the future.

Colour and colorimetric analysis

The classification of colour and aesthetic aspects of wood products or in this case of treated wood samples is subjective. An objective rating is difficult as personal opinions are differing with respect to colours. Therefore results are shown without judging the aesthetics of treated samples. Colours were classified in comparison to the colour of untreated spruce instead and relative changes to untreated spruce reference samples were assessed by application of a colorimetric analysis. Best rating in this case is reached for the treatment that causes the smallest colour change.

Oil-, temperature and pressure effect

Visibly, no difference in colour between RSO and LSO application can be observed. The darkening of the wood is clearly dependent on the temperature and the amount of oil uptake. Figure 6 shows a diagram in which colour co-ordinates can be determined and visualised. The positions of the measured samples show, how the colours were affected by the treatments. The L* a* b*- values were used to determine the position of each treatment in the chromaticity diagram.

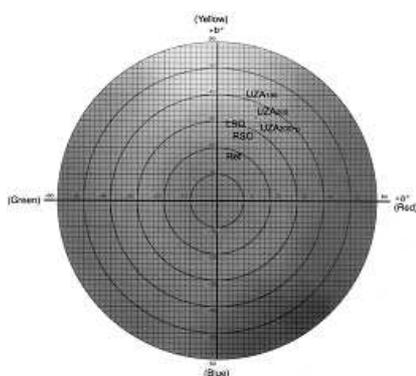


Figure 6: Positions of samples in the a*, b* chromaticity diagram (Minolta®)

As can be seen treatments changed colour in red and yellow directions (results in brown). UZA 180 samples changed clearly more to yellow than to red. This and the reduced darkening are clearly related to the lower temperature.

The visible impressions derived by optical assessment of the colour are found to be analogous to the colours expressed by the colorimetric values. Values of RSO and LSO are nearly the same and so are the positions in the diagram. The brightness (L^*) is reduced by all treatments. The most by UZA 200 + pressure, the least by UZA 180.

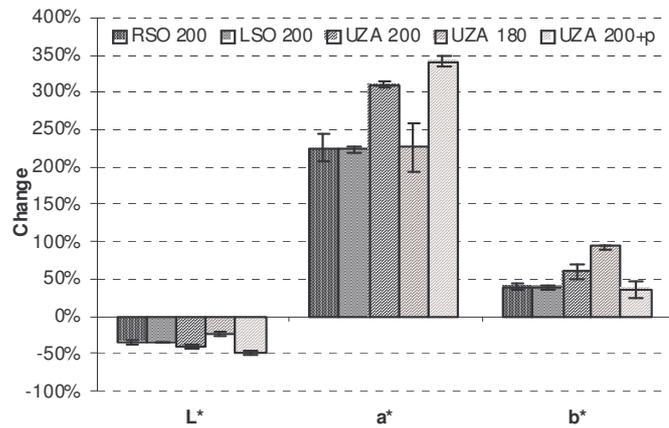


Figure 7: Changes of L^* , a^* , b^* values caused by treatments compared to reference.

The changes compared to reference are clearer when presented by relative changes. Figure 7 shows, that brightness is reduced up to 50% (UZA 200 + pressure). The greatest change to red is caused by UZA 180 (341%) and the greatest in yellow direction by UZA 180 (93%). The smallest changes are caused by RSO and LSO, L^* -35%, a^* + 225%, b^* +39%. Only brightness (L^*) is reduced by UZA 180 less than by RSO and LSO.

Elasto-mechanical changes

Oil effect (RSO 200, LSO 200, UZA 200)

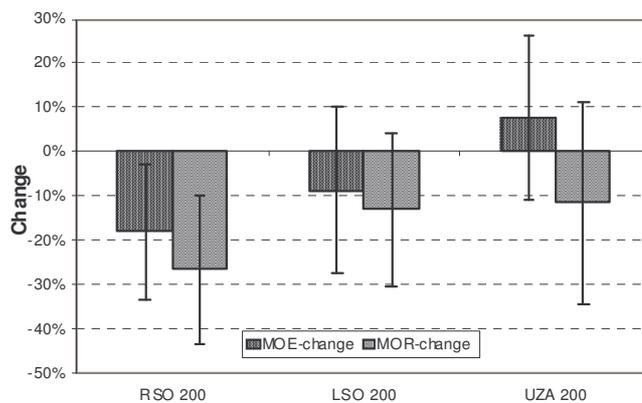


Figure 8: Static MOE- and MOR-change as a result of the treatments.

Changes in modulus of elasticity after oil-heat treatment are clearly dependent on type of oil as MOE is reduced after application of RSO (-18.2 %) and LSO (-8.8 %), but increased in case of the UZA 200 (7.7 %). The most important trend that is clearly recognisable is a growing reduction of MOE by use of RSO. The outcomes concerning LSO correspond to earlier studies by Sailer *et al.* (2000) who found slight reductions in MOE of treated spruce and pine, using refined linseed oil. Others reported a slight enhancement of MOE after oil-bath applications, using temperatures from 180°C to 220°C (Leithoff and Peek 2001). The enormous decrease of MOE using RSO may be related to the non-oxidising property of this oil. In general, high standard deviations were observed in this study making a clear interpretation of the results difficult. In this context the problem of high variations in strength measurements is known and often reported (Sailer *et al.* 2000, Syrjänen and Kangas 2000, Leithoff and Peek 2001).

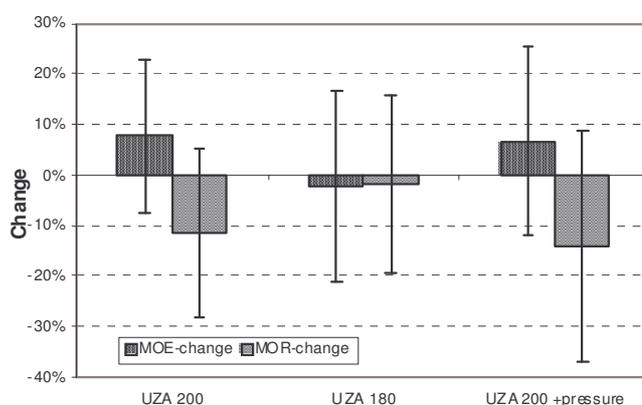


Figure 9: Static MOE- and MOR-change as a result of the treatments.

The modulus of rupture (MOR) was decreased by application of oil-heat treatments. LSO 200 and UZA 200 caused a reduction of approx. 12%. RSO 200 caused the MOR to decrease more than twice as much, approx. 27%. Again, it can be suggested that this difference is due to the missing oxidation of RSO. Generally it is well known that heat treatments lead to a decreasing strength of wood, since this is highly dependent on type of treatment. Losses in strength up to 50% or more by dry heat applications (oxygen) are reported (Seborg *et al.* 1953; Davids and Thompson 1964; Giebler 1983). In a later study by Militz and Tjeerdsma (1998) MOR of heat-treated Scots pine was found to be reduced by 20% only, using a two step treatment. However, strength losses as a result of the used treatments are undesired but cannot be prevented totally. Using UZA and LSO, strength loss can be minimised to in this set-up maximum average of 12 %.

Temperature and pressure effect (UZA 200, UZA 180, UZA 200+pressure)

A trend can be observed that with applying 180°C using UZA, MOR-loss can be reduced compared to an application of 200°C (Figure 9). Both, MOE as well as MOR seem to be little affected by UZA 180°C treatment. Earlier reports by Tjeerdsma and Militz (1998), Sailer *et al.* (2000), Syrjänen and Kangas (2000), Leithoff and Peek (2001) and Yildiz *et al.*

(2002) found that elasticity and strength of various wood species were slightly decreased with increased temperature, what is more or less corresponding to the outcomes of this study. An application of pressure during the heating phase of the process, does obviously not influence the changes in strength and elasticity. Only negligible differences between UZA 200 with and without pressure can be observed.

CONCLUSIONS

Joint efforts of industry and research institutes have resulted in the development of an improved thermal treatment with reactive vegetable oils. This work has led to the development and implementation of modified hot-oil for use in the modification of wood at pilot-scale production stage. In this treatment the modified oil combines the traditional thermal treatment of wood with chemical modification. Wood with altered properties resulting from both types of treatment is produced by this novel process.

Oil effect (RSO, LSO, UZA)

The results showed that colour and elasto-mechanical properties were affected by the applied oil-heat treatments and that the extent of changes is depending on type of oil used during the process. Colour was affected by UZA in a greater extent than by RSO and LSO. In particular the brightness was reduced more using UZA. Treatment with RSO and LSO resulted in the same colour and the same L* a* b*- values. The difference between the (plain) heat treatment in RSO compared to the treatment in the reactive linseed oil (UZA), indicates the extra effect on improving the durability in the reactive oil treatment compared to a “plain” heat treatment. A serious disadvantage of RSO was the enormously decreased MOR. Treatment with RSO resulted in a MOR-loss of 26.7%. The effect of LSO treatment (13.2%) and especially of UZA treatment (11.7%) in this context was half compared to the RSO treatment. Analogous results have been observed for MOE-reduction caused by the treatments.

Temperature and pressure effect (UZA)

By applying 180°C instead of 200°C during the process using UZA, changes in, colour and decrease in elasto-mechanical properties can be considerably reduced. The outcomes of colorimetric analysis showed that losses in brightness can be halved when 180 °C is applied, and finally MOR-loss was substantial higher using UZA 200°C (11.7%) compared to treatment in UZA 180°C (2.0%). With respect to the durability a clear temperature effect can be seen, were the 180°C treatments show minor effect compared to the higher temperature treatments. Pressure (9 bar) during the treatment process resulted in a higher weight percent gain. Brightness of the colour was further reduced compared to UZA without pressure. No effect was found on MOR/MOE- changes.

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Laboratory and Field Tests of the Anti-marine Borer Potential of Wood Modified with Dimethyloldihydroxyethyleneurea (DMDHEU) and Phosphobutane Tricarboxylic acid (PBTC)

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Keywords: *Limnoria*, modified wood, screening test, field trials, marine borer, DMDHEU, DHDMI, PBTC

ABSTRACT

Treatments using a combination of dimethyloldihydroxyethyleneurea (DMDHEU) and phosphobutane tricarboxylic acid (PBTC) were applied to the non-durable timbers *Pinus sylvestris*, *Pinus radiata* and *Picea* sp. Laboratory screening tests and field trials assessed the marine borer resistance of these modified woods. The field trials were conducted in a site of high limnoriid and teredinid borer activity (Olhão, Portugal) for a period of 12 months. In the laboratory trials, the production of faecal pellets by the wood-boring isopod crustacean *Limnoria quadripunctata* was measured under forced feeding conditions. Activity and mortality were also recorded. Mortality was high on some treatments. On others, pellet production rate was much lower than on untreated wood. For some treatments, there was evidence of antifeedant effects. The field trial panels were X-rayed to assess the severity of attack and cut up to extract specimens for borer identification. Field and lab trials showed similar results. DMDHEU in combination with PBTC showed good results against limnoriids and teredinids. The timber treated with DHDMI (dihydroxydimethylimidazolidinone) showed good resistance against limnoriid attack.

INTRODUCTION

Trials of early chemical modification processes showed that modification may prevent marine wood borer attack (Johnson and Rowell 1988). However, the established test methodology (e.g. EN 275) takes a long time, using large samples and thus is costly and slow. A screening bioassay under development (Borges *et al.* 2004) is evaluated in this study of various wood modifications, with laboratory findings being validated by comparison with a marine trial.

EXPERIMENTAL

Test sticks with dimensions 20 x 4.5 x 1.5 mm were machined from modified *Pinus sylvestris* sapwood prepared as described by Borges *et al.* (2004) and then subjected to one week leaching in seawater prior to laboratory testing. For field testing, the five chemical modification treatments detailed in Table 1 were each applied to ten replicate panels (200 x 150 x 20 mm) of *Pinus sylvestris*. The treatment solutions were adjusted to pH 2.5 using ammonia. The panels and solutions were subjected to 30 minutes vacuum then 1 hour at 8 bar pressure. Panel weight gain was measured. Panels were dried at 30°C for 3 days then cured at 120°C for 16 hours.

A test stick (twelve replicates per treatment) and an adult wood-boring isopod (*Limnoria quadripunctata* Holthuis) were placed in each

chamber of a cell culture box immersed in seawater maintained at $20\pm 2^\circ\text{C}$. The box was covered with plankton mesh held in place by a lid that had circular holes to permit water circulation into each chamber. The faecal pellets produced after one and two weeks were counted, and dead, inactive, and moulting animals were recorded.

The treated panels plus panels of untreated *P. sylvestris* and *Picea* sp. were exposed in Olhão harbour, Ria Formosa Lagoon, Portugal. They were suspended on a vertical nylon rope between 1 and 2 m below low tide, with the larger dimensions of the panels horizontal. After a year, the severity of attack was assessed according to EN 275 and the borer species present were identified.

RESULTS AND DISCUSSION

Laboratory test

Survival rate varied greatly with treatments, with some causing 90 % mortality, while all animals survived on untreated wood (Fig 1).

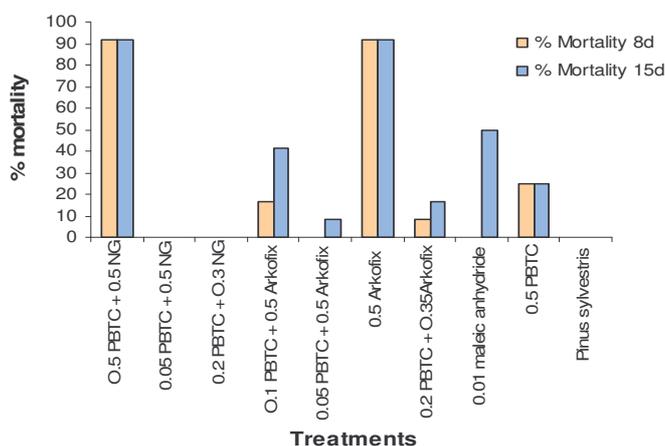


Figure 1. Percentage of mortality in *Limnoria quadripunctata* in contact with different chemical modification treatments, after 8 and 15 days.

Both treatment type and period of exposure significantly affected pellet production rates ($p < 0.01$, GLM ANOVA with treatment and period as fixed factors). The formulation 0.2 M PBTC + 0.5 M Arkofix was non-toxic to the animals but suppressed feeding significantly when compared with untreated Scots pine, suggesting an antifeedant effect. Reduced feeding on modified substrates in the second week could be due to modification affecting binding sites and thus reducing the efficacy of the putative cellulase identified by Dymond *et al.* (2003). Alternatively, the modifications may have a chronic sublethal effect.

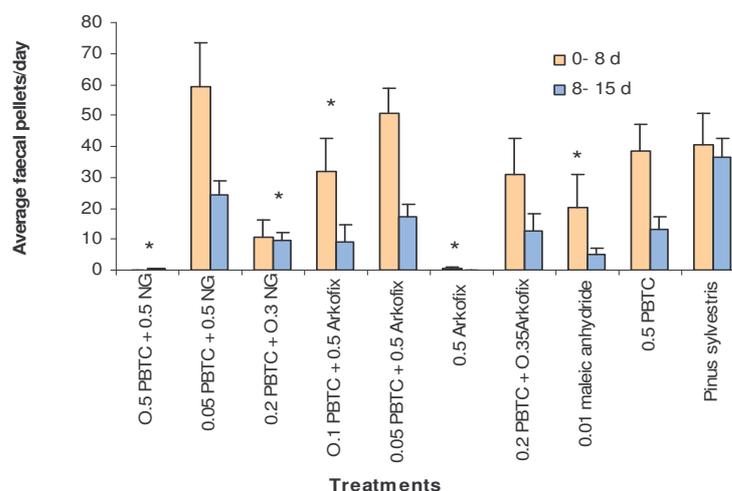


Figure 2. Effect of treatment on rate of faecal pellet production by *Limnoria quadripunctata* over a period of time of 8 and 15 days. Treatments are expressed in molarity. Asterisk indicates treatments with significantly lower rate than Scots pine (Dunnet's test $p < 0.05$).

Field trial

Borer activity at Olhão was very high with untreated panels failing in less than a year, mainly due to *Limnoria tripunctata* and the shipworm *Lyrodus pedicellatus* (Table 1). However, panels treated with 0.05 M PBTC + 0.05 M DMDHEU showed a very good resistance both to teredinids and limnoriids (Table 1). In previous lab tests with *Limnoria quadripunctata* this treatment also performed well, showing an 85% suppression of the feeding rate when compared to Scots pine (Borges *et al.* 2004) The modified wood did not suppress the tunnelling, as all panels showed some slight attack. The panels treated with 0.05 M PBTC showed moderate resistance to teredinids and limnoriids in the field, but were attacked in the laboratory test. Maleic anhydride-treated wood performed well in the laboratory, but not in the field. The other treatments were attacked in both field and laboratory conditions.

Table 1. Wood treatments used in the field trials. Wood boring species and severity of attack in the test panels exposed in Olhão harbour, Portugal. 0-no attack; 4-maximum severity of attack.

Treatments (molarity)	Bivalves		Crustaceans		Severity of attack	
	<i>Lyrodus pedicellatus</i>	<i>Teredo bartschi</i>	<i>Limnoria tripunctata</i>	Molluscs rating	Crustaceans rating	
<i>Pinus sylvestris</i> acetylated	x	x	x	2.5	0.8	
<i>P. sylvestris</i> + 0.05 PBTC	x	x	x	1.5	1.5	
<i>P. sylvestris</i> + 0.01 DMDHEU	x		x	2	1.2	
<i>P. sylvestris</i> + 0.05 PBTC + 0.05 DMDHEU	x		x	<1	<1	
<i>P. sylvestris</i> + 0.01 maleic anhydride	x	x	x	2.3	4	
Untreated <i>P. sylvestris</i>	x		x	3.8	4	

CONCLUSIONS

Results from field and on lab trials showed good potential for PBTC alone and in combination with DMDHEU for marine use. Laboratory results gave, in most cases, a good prediction of field performance.

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Properties of Wood Following Treatment with a Modified Hot Oil

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Keywords: Modification, oil-heat treatment (OHT), properties

ABSTRACT

The reaction of European timber species with a reactive oil (UZA) at elevated temperatures has been developed and is being implemented on a semi-commercial scale. Evaluations of the oil and subsequent treatments have been carried out, which show that the oil has reactive sites chemically bound to the fatty acid chains within the oil. This allows the oil to act as a chemical modification agent, whilst the elevated temperatures result in a thermal treatment process. Assessment of treated timber showed dramatic improvements in the durability, slight to moderate reductions in mechanical properties, and reduced moisture uptake. Chemical assessment of the UZA suggests the maleic anhydride reactive group has chemically bound to the unsaturated groups of the fatty acids present.

INTRODUCTION

This work was carried out within the framework of an European Craft project entitled Ecotan (QLK5-CT2002-72467), aimed at the development of a commercially feasible process incorporating reactive oils and thermal modification. Sailer *et al.* (2000) demonstrated the potential for oil-heat treatments, such that there are now several initiatives across Europe assessing the potential of such processes. The drive for such a process is to provide biocide-free treatments for the enhancement of sustainably grown European timbers, which may then compete favourably with higher value imported species. This paper follows on from work presented by Tjeerdsma *et al.* (2005), whereby a chemically active group has been incorporated into the oil matrix.

EXPERIMENTAL

Samples of wood of various European species were treated at SHR, Netherlands using their MP2 reactor (Figure 1). Ecotan 12 and 13 refers to experiments where the reactive oil (UZA) has been used during impregnation and heating, whilst Ecotan 14 and 15 used linseed oil for heating following impregnation with UZA. The treated material was then returned for the following testing.

Weight uptake – Samples were immersed in water over a period of 72 hours, during which time regular weighing was carried out. Results were calculated in terms of weight increase against over dry weight of the sample.

Biological durability - This was determined according to standard methods, namely EN350-1, CEN TC35 WG23 N34, ENV807 and EN252.

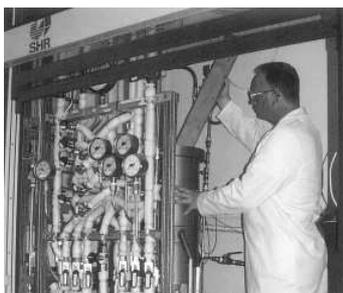


Figure 1: MP2 reactor at SHR, Netherlands

Mechanical properties – Mechanical properties (MOE, MOR) were assessed according to 3-point bending measurements and impact testing according to falling weight as defined in BS373 (1957).

Chemical assessment – The composition of the oil was carried out as required for Fourier Transform- Infra Red (FT-IR) Spectroscopy, ^{13}C and ^1H NMR Spectroscopy and Mass Spectrometry.

RESULTS AND DISCUSSION

Some properties of timber treated using this modified hot oil process has already been reported (Tjeerdsma *et al.* 2005). The results that follow compliment these findings.

Weight and water uptake

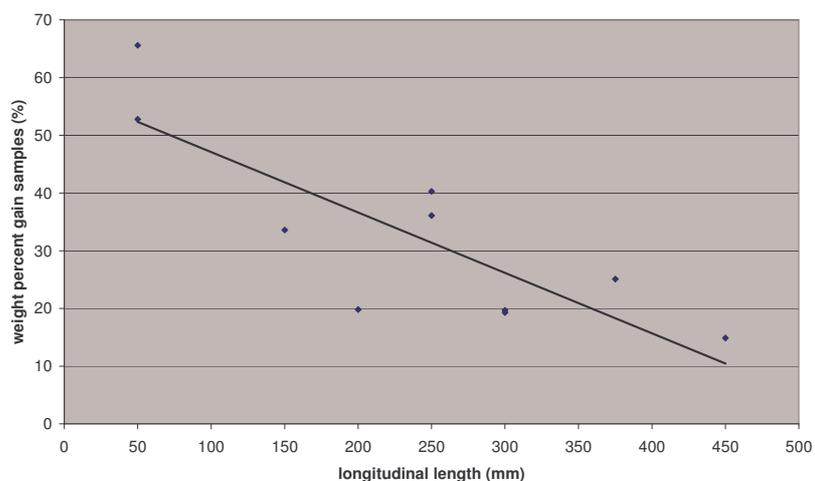


Figure 2: Weight uptake relationship to longitudinal length for Sitka spruce

Experiments with Sitka spruce of varying dimensions allowed the relationship between the longitudinal length of samples and the overall Weight Percent Gain (WPG) observed (Figure 2) to be derived. This showed that longer samples have lower WPGs, which may be attributed to limited penetration through the radial and tangential directions, or along the whole longitudinal lengths. Tests were also carried out to assess the uptake of water (in terms of % weight increase) related to the hot oil treatment. Thus samples (both treated and controls) that had been oven-dried prior to testing, were immersed in water, and their weights measured over an interval of several days. Figure 3 shows graphically how the overall percentage weight increased for both sets of blocks.

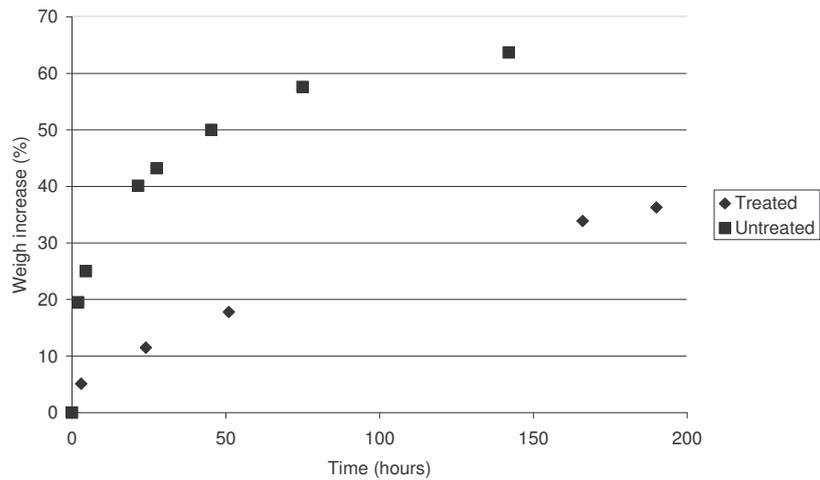


Figure 3: Percentage weight increase due to water uptake

Biological durability

Tests were carried out using samples as obtained from the treatment vessel (hereafter referred to as unsanded), as well as on blocks that had the polymerised coating removed (sanded). Experiments were carried out to determine the level of improvement in the durability of the treated timber according to EN113 protocol, for sanded and unsanded material. In all cases, Norwegian spruce was evaluated. The results achieved (Table 1) could then be assessed according to EN350-1 and N34 respectively.

Table 1: Biological durability ratings of EN113 samples according to EN350-1 and N34 respectively.

Treatment	Weight loss	Weight loss	Durability rating N34	Durability rating EN350-1
	C. puteana [%]	P. placenta [%]		
Ecotan 12 sanded	0	3.41	1	1
Ecotan 12 Unsanded	0	0	1	1
Ecotan 13 Sanded	0.49	1.04	1	1
Ecotan 13 Unsanded	0.07	0.25	1	1
Ecotan 14 Sanded	5.41	5.14	2	2
Ecotan 14 Unsanded	6.52	4.59	2	2
Ecotan 15 Sanded	4.90	4.67	1	2
Ecotan 15 Unsanded	4.79	3.95	1	2
Spruce controls	34.70	22.76	5	5
Pine controls	34.84	23.73	5	5

These results show that good durability could be achieved both with sanded and unsanded samples. There was a slight decrease in the level of protection afforded with the sanded samples, but this would be explained by the removal of the protective polymer coating produced by the reacted oil. Its removal provides a more realistic view of the effect of the oil treatment on the interior of the blocks.

In addition to experiments to determine the natural durability, work was also carried out using ENV807 test standard (laboratory based) as well as EN252 (field test based). EN350-1 suggests that currently it is not possible to give any guidance as to the natural durability of modified timber based on an ENV807 test. Work on new standards by CEN

TC38/WG23 has suggested applying methodologies developed within EN350-1 for interpreting data from ENV807 tests, which would include assessing mechanical properties for softwood species. However, direct mass losses will be used in this evaluation, as the treatments used for the supplied timber have not been optimised. These showed that the presence of the polymerised reactive oil on the surface (unsanded samples) had greater resistance in ground contact. The use of UZA during the heating stage also provided additional protection, compared to linseed oil, with weight losses following ENV807 testing of 1 to 3 % and 7 to 10 % respectively as opposed to 24 % weight loss from control samples (all tested over a 32 week period). Field test stakes, according to EN252 show similar degrees of improvement in decay resistance.

Mechanical properties

Tjeerdsma *et al.* (2005) referred to moderate strength losses following treatment with UZA, with MOE and MOR typically reduced by approximately 10 %. However, these reductions were greater with the use of rape seed oil for the heating process. Similar results were noted (Table 2), when considering treatments where linseed oil was used during the heating stage.

Table 2: Overview of mechanical properties.

Treatment	MOR [Nmm ⁻²]	Std. dev. [Nmm ⁻²]	MOE [Nmm ⁻²]	Std. dev. [Nmm ⁻²]
Untreated	84	14	13500	2600
Ecotan 14	63	12	12300	3400
Ecotan 15	70	18	13600	1700

It was also noted that the impact strength of the hot-oil treated timber was greatly reduced, with reductions of approximately 50 %. Further studies into this will be carried out to determine if variations in the treatment can limit this reduction.

Chemical analysis

Fourier Transform Infra-Red Spectroscopy (FTIR)

FTIR was used to investigate the nature of the covalent bonds between carbon, hydrogen and oxygen within the oil and the resin. Absorptions characteristic of an anhydride were seen in the spectrum for UZA, which were not present in that for linseed oil. This was as expected, and showed that the ring structure of the maleic anhydride has not been degraded during the reaction. The polymerised skin of UZA from the pressure reactor was observed by FTIR and the presence of oxygen was strongly detected in the region above 3000 cm⁻¹ and 1500 to 1000 cm⁻¹. It is anticipated that polymerisation occurs by some oxidative cross-linking process, which is a free radical mechanism.

Nuclear Magnetic Resonance Spectroscopy

Proton (¹H) and carbon 13 (¹³C) spectra were obtained for the linseed oil and UZA. The proton spectra for linseed oil and UZA were very similar. They showed protons in CH₃ and CH₂ environments at 0.9 to 1.0 ppm and 1.3 to 1.4 ppm respectively. Other multiplets were observed at 2.1-2.8 ppm and 4.1- 4.3 ppm, which are likely to relate to methene groups. Rao *et al.* (1996) reported similar observations for maleic anhydride adducts of linseed oil.

The linseed oil ¹³C spectrum showed peaks in all the expected locations, with subtle variations between the palmitic, stearic and oleic acids, as

expected. The UZA spectrum was almost identical to the linseed spectrum, although there was a small peak in the 45 ppm area which was almost lost in the noise of the spectrum baseline. If this peak is significant it could indicate the presence of Diels-Alder type ring structures.

Mass Spectroscopy

Direct insertion mass spectroscopy was used to detect molecular ions of linseed oil and UZA. For linseed oil there are an anticipated set of 35 molecular ions as the oil contains five different fatty acids within the triglyceride. The molecular ion region contained five strong masses relating to the main triglycerides present, but also contained five medium-strong masses relating to isotopes of the carbon and hydrogen. Further, there were also many low intensity masses detected relating to triglycerides with a lower abundance in the oil. Two distinct regions contained molecular ions: from 872.6 to 882.7 the ions relating to non-palmitic fatty acids were present; and from 844.7 to 858.7 the palmitic fatty acids were present. The molecular ions had lost a single CH₃ unit. The palmitic molecular ion region also contained non-palmitic ions which had lost larger fragments or a pair of CH₃ units.

Whilst molecular ions for the unreacted fatty acids were noted, none were present representing the maleated product. However, there was an absence of unsaturation from the degradation patterns. This does suggest reaction has occurred. Model compounds (such as linoleic acid) were grafted with maleic anhydride and tested by mass spectrometry. This showed unreacted acids, whereas linolenic acid showed the presence of a maleated compound. Thus it would appear that only some model compounds readily produce molecular ions. However, the absence of unsaturation would suggest the fatty acids have been modified.

CONCLUSIONS

The use of reactive oils such as UZA can afford European timbers with dramatic improvements in many properties. This may open markets hitherto inaccessible to such timber species. Further determinations into assessing any detrimental effects needs to be carried out so that these are limited. This will allow greater potential for multiple market entry. As reported by Tjeerdsma *et al.* (2005), semi-commercialisation of this process is already underway, and represents an exciting development in the use of oil and heat treatments.

ACKNOWLEDGEMENTS

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Enhanced Durability of Scots Pine Wood Resulting from Treating with Modified Alkyd Resin

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Keywords: Alkyd resin, biocides, durability, impregnation, pine, tests

ABSTRACT

High resistance to various biological organisms action and abiotic factors is required of wood used outdoors. Impregnation of wood with chemical preservatives can prevent wood from deterioration and extend its service life. Some preparations very often include organic solvents which pollute the atmosphere, which is why development of new chemicals or preparations with low mammalian toxicity and less danger to the environment is still the main goal of much research and a possible solution could be water solvent wood preservatives based on resins and containing biocides. The objective of this study was to determine, by laboratory accelerated methods and field tests, the effectiveness of water diluted alkyd resin modified with biocides (triazole, IPBC, cyfluthrine) against wood destroying basidiomycetes (screening test on EN 113 basis) and against fungi causing blue-stain in service (EN 152-1) as well as to determine the increase in wood durability in contact with the ground (EN 252). Scots pine wood *Pinus sylvestris* L. was used for tests. In the case of *Coniophora puteana*, the toxic values of the preparation amounted to about 2 kg/m³ before leaching and about 3 kg/m³ after leaching, which means full (adequate) resistance of treated wood to *Coniophora puteana*. The resistance of wood treated on the surface with the preparation against blue-stain in service (*Aureobasidium pullulans* and *Sclerophoma pityophila*) was rather good – the depth of the blue-stain free zone was about 3.6 mm. Also in ground contact during a 5-year field test high resistance of the wood treated with water dilutions of modified alkyd resin in concentrations of 20 %, 33 % and 100 % was found. Thus, the preparation may prove useful for the long-term preservation of wood, probably also in contact with the ground. This treatment has been used for the preservation of wooden ground beams of the XVIth century wooden church.

INTRODUCTION

Wood is vulnerable to attack by biological organisms: bacteria, fungi, insects, marine borers and abiotic factors: chemical, physical, mechanical. Impregnation of wood with chemical preservatives can prevent wood from deterioration and extend its service life. Development of new chemicals or preparations with low mammalian toxicity and of less danger to the environment is the main goal of much research. Decorative - impregnation preparations very often include an organic solvent which pollutes the atmosphere. This deficiency does not occur in the case of water solvent wood preservatives. A preparation soluble in water and effective as wood preservatives will probably be widely used in the future. Environmentally-friendly impregnation using water as a solvent in certain situations can be used to treat archeological wood too (Fojutowski 2002).

The objective of this study was to determine, by laboratory accelerated methods and field testing, the effectiveness of water diluted alkyd resin modified with biocides (triazole, IPBC, cyfluthrine) against wood destroying basidiomycetes (screening test on EN 113 basis) and against fungi causing blue-stain in service (EN 152-1), as well as to determine changes in wood durability in contact with the ground (EN 252).

EXPERIMENTAL

Triazole preparation (T): milky-white liquid with only a very weak odour of alkyd resin. Composition type of alkyd resin emulsion in water; biologically active ingredients: Tebuconazole, propiconazole (triazole group compounds with good known fungicidal activity) – effective against wood against fungi causing brown and white rot of wood; IPBC - effective against blue-stain fungi; Cyfluthrine: a synthetic insecticide from the pyrethroide group with a wide range of action against insects (Fojutowski and Krajewski 1998, Valcke and Stevens 1991).

Comparative preparation (C): equivalent of T preparation but without active ingredients; used as a control in blue- stain investigation

Reference preparation (R): wood preservative used in blue-stain investigation; oil-organic solvent type; transparent and colourless; active ingredients: tebuconazole 0,6%, dichlofluanid 0,5%, permethrine 0,03%.

The resistance of the treated wood against wood destroying basidiomycetes was determined by the screening agar - block test on the basis of EN 113 and earlier work (Fojutowski and Zieliński 1986, Wałny and Krajewski 1994, Zabielska - Matejuk 1997). Wood specimens of Scots pine sapwood (*Pinus sylvestris* L.): 22x17x12mm, a special nutrient medium were used in the test. An inherent part of the test was a 4-week incubation period with *Coniophora puteana* (strain BAM 15). Toxic values of the T preparation were determined on wood samples after a cycle of leaching according to a standard method (EN 84) and also without the cycle of leaching. Wood samples were saturated with dilutions of the T preparation of concentrations: 0.016, 0.025, 0.04, 0.063, 0.1, 0.16, 0.25 and 0.4 %.

Resistance of wood treated with the T preparation to blue-stain in service was determined using a standard test method (EN 152-1) in combination with artificial weathering according to American standard (ASTM D 2898-94(99) which substituted natural, external, field weathering described in EN 152-1. The T and C preparations were used according to a brushing procedure in quantities of 100, 150 and 200 g/m² and the R preparation in a quantity of 200 g/m². The following fungi were used: *Aureobasidium pullulans* de Bary (Arnoud) and *Sclerophoma pityophila* (Corda) v. Höhn. Artificial weathering of preserved wood samples was as follows: 24 h exposure cycle consisting of 4 h wetting (artificial rain), 4 h drying (temp.63±3°C, air movement and ultraviolet light), 4 h wetting, 4 h drying, 8 h rest. The cycle was repeated 20 times for a total time of 480 h. This represents a simulated 15-year exposure in Houston, Texas, USA with an average annual rainfall of 1140mm.

A standard method (EN 152-1) was used for testing durability in contact with the ground of wood vacuum treated with water dilutions of the preparation T of concentrations: 0, 20, 33 and 100 % with Scots pine

sapwood samples: 450 x 55 x 20 mm. Visual evaluation was used from – without attack signs, by 1 – weak attack to 4 – damage.

RESULTS AND DISCUSSION

Scots pine sapwood with the T preparation retention varying from 1.22 to 1.91 kg/m³ (by the graphic method – 1.8 kg/m³), without leaching, proved to be resistant to decay caused by *Coniophora puteana*, and the same could be observed when retention varied from 1.92 to 3.05 kg/m³ after leaching (by the graphic method – 2.6 kg/m³). These indicate high fungicidal activity of the T preparation. The leaching coefficient was only 1.8. The fixation of the T preparation in wood was good and higher than some of the QAC compounds presently considered as ecological composition (Figure 1, Table 1).

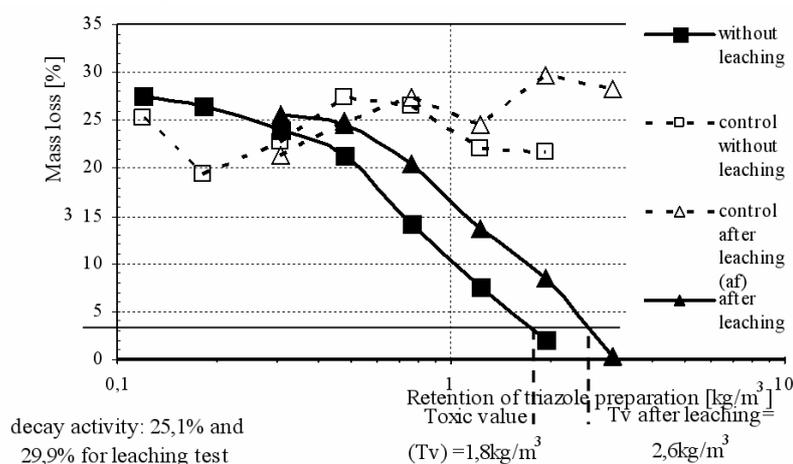


Figure 1: Toxic values of triazole preparation to *Coniophora puteana* in the Scots pine sapwood-screening test

Table 1: Resistance of the T preparation treated Scots pine sapwood to *Coniophora puteana*

Toxic values			Leaching	
Solution concentration [%]	according to EN 113		PN-C-04903	PN-C-04908
	Preservative retention [kg/m ³]	Mean corrected mass loss at the highest failing concentration [%]	Preservative retention [kg/m ³]	Leaching coefficient
a) without leaching				
0.16-0.25	1.22-1.91	7.7	1.8	-
b) after leaching acc. to EN 84				
0.25-0.40	1.92-3.05	8.5	2.6	1.8

During artificial weathering, occurrence of blue-stain did not take place (Figures 2 and 3). The surface of the wood samples treated with the preparations T or C changed from yellow to grey-yellow giving a good, aesthetic appearance. The surface of the control wood samples and the samples treated with the reference preparation R

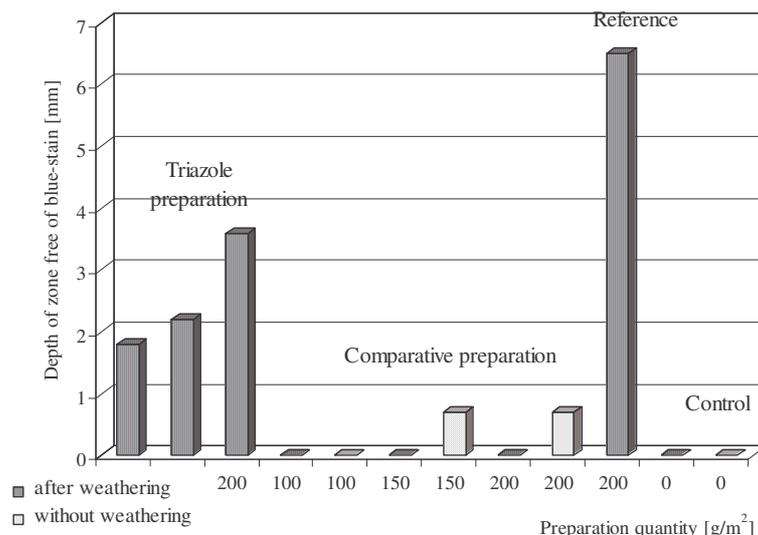


Figure 2: Effectiveness of triazole preparation against blue-stain fungi action acc. to PN-EN 152-1. Depth of the blue-stain free zone in service on wood samples cross section

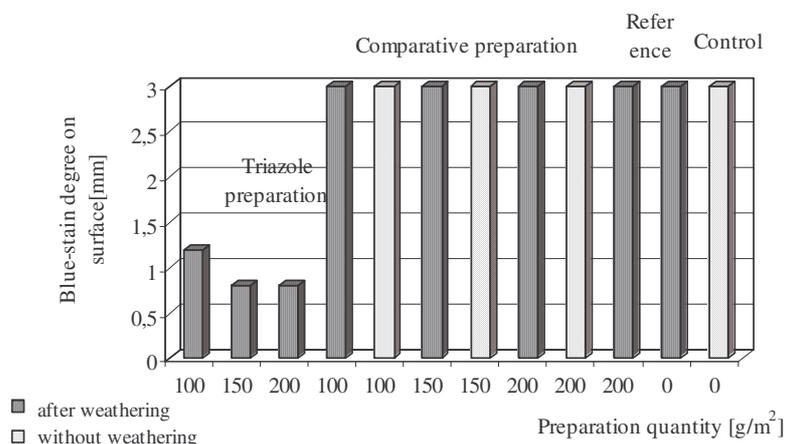


Figure 3: Effectiveness of triazole preparation against blue-stain fungi action acc. to EN 152-1. Blue-stain degree on wood samples surface

changed to greyish. The T preparation in successive laboratory tests with fungi causing blue-stain in wood indicated a good preserving action (average blue-stain infection degree on wood samples surface was about 1 = traces, and the depth of the blue-stain free zone on cross section was: 1.8 mm for 100 g/m², 2.2 mm for 150 g/m², 3.6 mm for 200 g/m²). The comparative preparation C did not preserve wood samples against blue-stain in service even at 200 g/m² (blue-stain degree was 3 = strong attack by blue-stain on all surfaces, all cross section blue-stained - lack of the blue-stain free zone). Change in the control (non treated) wood samples was similar to that on wood treated with the C preparation. The surface of the wood samples treated with the reference preparation R was grey (average blue-stain infection degree was 3) but the depth of the blue stain free zone was the greatest – 6.5mm. The results of field test shows (Figure 4) the high durability of treated wood in contact with ground in comparison to untreated – control wood even by the lowest (20 %) concentrations of preparation T.

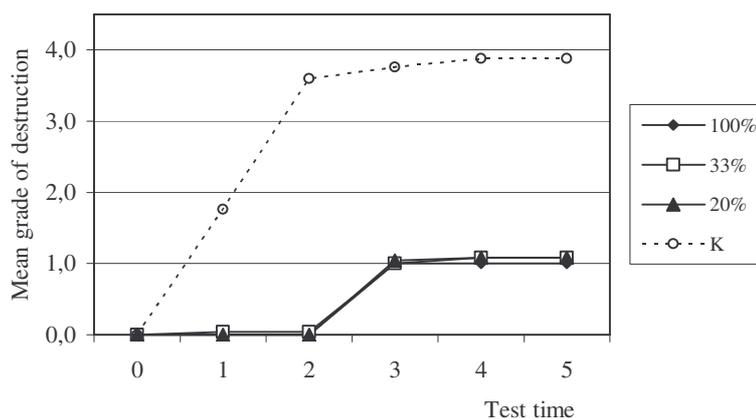


Figure 4: Mean values of destruction degree (visual evaluation) of wood treated with triazole preparation of different concentrations and control samples in succeeding test periods

CONCLUSIONS

The Scots pine wood treated with preparation T based on alkyd resin and tebuconazole, propiconazole, IPBC, cyfluthrin indicated good resistance against fungi causing brown rot and blue-stain in service, high durability during the simulated 15-year exposure without contact with ground and in contact with ground during 5 years of field test. The wood modified with above mentioned preparation T may occur useful for long term preservation of wooden elements inside and outside.

ACKNOWLEDGEMENTS

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EN 151-1 Test methods for wood preservative – Laboratory method for determining the protective effectiveness of a preservative treatment against blue stain in service – Part 1: Brushing procedure.

EN 252 Wood preservatives – Field test method for determining the relative protective effectiveness of a wood preservative in ground contact.

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CHAPTER 4

SILICONES

CHEMICAL GRAFTING OF REACTIVE TRIETHOXY-SILANE END GROUPS IN MARITIME PINE SAPWOOD (*PINUS PINASTER SOLAND*)

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Keywords: Chemical modification; 3-isocyanatopropyltriethoxysilane; silicon; wood

ABSTRACT

The chemical modification of maritime pine sapwood (*Pinus pinaster Soland*) with 3-isocyanatopropyltriethoxysilane (IPTES) and its subsequent hydrolysis were investigated. The carbamoylation reaction was confirmed by SEM-EDX, FTIR and CP-MAS ¹³C NMR analyses. Hydrolysis of the grafted triethoxysilane ends was also performed and the modifications characterised. The new silicon structures found in wood were further determined by CP-MAS ²⁹Si NMR analysis. The formation of silanol groups and other condensed structures was particularly evident after hydrolysis.

INTRODUCTION

The chemical modification of wood with organosilicon molecules has received increasing attention over the last decade and various wood properties such as dimensional stability, moisture uptake, weathering, fire resistance or durability have been improved after treatment with such compounds (Hill *et al.* 2004, Mai and Militz 2004, Sèbe and de Jéso 2000, Sèbe and Brook 2001, Sèbe *et al.* 2004). The chemical modification of wood with 3-isocyanatopropyltriethoxysilane (IPTES) is particularly attractive, due to the bifunctional nature of the silane molecule: the carbamoylation reaction between wood hydroxyl groups and the isocyanate function offers the possibility to introduce reactive triethoxysilane end groups in wood. These groups can be easily hydrolysed into silanol groups, which are highly reactive with regards to other silanol molecules (possibility to anchor hydrophobic moieties from these sites).

The carbamoylation reaction between wood hydroxyl groups and IPTES was thus performed and the modifications characterised by FTIR, solid state NMR (¹³C and ²⁹Si) and SEM-EDX analyses. The reactivity of the grafted triethoxysilane ends with regard to hydrolysis was subsequently studied.

EXPERIMENTAL

Wood treatment

3-isocyanatopropyltriethoxysilane (IPTES), dibutyltin dilaurate (DBTDL) and dimethylformamide (DMF) were used as received from Sigma-Aldrich. Maritime pine sapwood (*Pinus Pinaster Soland*) was used as a substrate. Prior to use, samples were Soxhlet extracted with toluene:ethanol (2:1/v:v) for 8 hours then with water for an additional 8 hours. After reaction (6h, 105°C), samples were again extracted (8h acetone + 4h dichloromethane) then dried (16h, 105°C). Carbamoylation

reactions (Figure 1A) were performed both on wood blocks (20 x 20 x 2.5 mm³: rad. x tang. x long.) and sawdust. After modification, the weight percent gain (WPG) as well as the radial and tangential swellings of the modified blocks (SR and ST) were calculated as percentage of dry, extracted wood. The following reagent solutions were used:

Wood blocks: 8 mmol IPTES/g dry wood in 70 ml DMF, with DBTDL as a catalyst (0.4 mmol DBTDL /g dry wood). A 26% WPG was obtained.

Sawdust: 400 μm wood particles were reacted with 14 mmol IPTES/g dry wood, in 25 ml DMF, with DBTDL as a catalyst (0.7 mmol DBTDL/g dry wood). Highly modified sawdust was obtained (138.5% WPG).

Hydrolysis of carbamoylated wood (Figure 1B) was performed by immersing samples in water, for 2 then 5 days, with stirring.

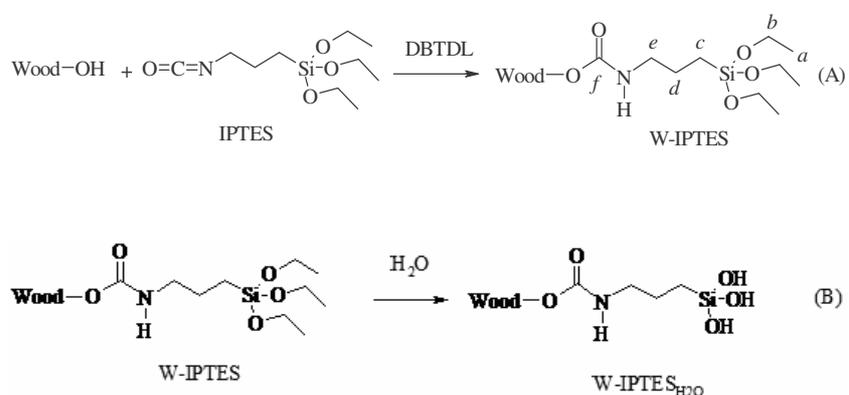


Figure 1: (A) Carbamoylation of wood with IPTES. (B) Hydrolysis of carbamoylated wood.

SEM-EDX analysis

The scanning electron microscopy studies were conducted using a Hitachi S-2300 SEM equipped with a Roentec-XFlash detector. The instrument operated at an acceleration voltage of 15 kV, 100 μA emission current and a working distance of 15 mm. The silicon of the IPTES molecule was identified in the EDX spectra at peak position K α 1.74 keV (K β 1.826), EDX peak window for ¹⁴Si was adjusted to 1.71-1.856 keV. The scanning rate for EDX mapping was 3ms/ 1 frame with a resolution of 512 x 384 pixels. The input rate of the detector was about 10³ -1.5 x 10³ cps (counts per second). 150-300 cps were observed for W-IPTES resulting in the silicon distribution image in Figure 2b. Wood blocks were water saturated (at 4°C) for 48 h. Afterwards the specimens were sliced in a freezing microtome Kryostat 2800 Frigocut-N (Reichert-Jung, Cambridge Instruments GmbH) at -22 °C. The shock freezing procedure prevented the formation of ice crystals and kept the shape of the cells. The slides exhibited an average thickness of 20 μm. They were directly glued onto graphite adhesive labels together with aluminium sample holders (Leit-Tabs) and stored overnight to allow careful drying.

Infrared spectroscopy

Infrared absorption spectra of treated and unmodified wood were obtained using the potassium bromide technique (KBr), using a Perkin-Elmer Paragon 1000 PC FT-IR spectrometer with a HLLT detector, at a resolution of 4 cm^{-1} (50 scans).

^{13}C and ^{29}Si NMR CP-MAS analysis

Solid state ^{13}C and ^{29}Si CP-MAS (Cross Polarisation - Magic Angle Spinning) NMR spectra of treated and unmodified sawdust were performed at room temperature on a Bruker DPX-400 NMR spectrometer, using MAS rates of 4 and 8 kHz, at a frequency of 100.61 MHz for ^{13}C NMR and 79.49 MHz for ^{29}Si NMR. Chemical shifts were relative to Tetramethylsilane used as external standard. All the spectra were run for 15 h.

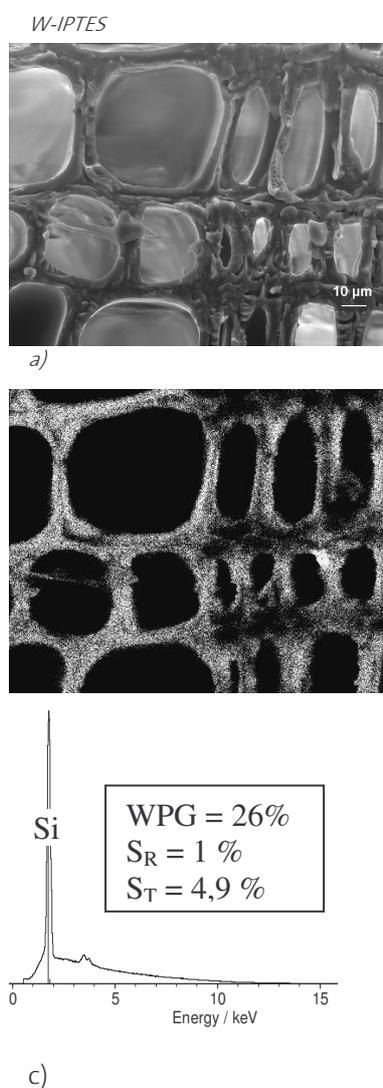


Figure 2: SEM micrograph of W-IPTES (a: mag. 800x). Silicon mapping (b) and the corresponding silicon peak in the EDX spectra (c) are shown.

RESULTS AND DISCUSSION

Carbamoylation reaction

After DBTDL-catalysed carbamoylation of wood blocks (Figure 1A), the following WPG and swellings were obtained: WPG = 26 %; $S_R = 1.0\%$; $S_T = 4.9\%$. The chemical swelling observed, mostly in the tangential direction, indicates clearly that grafting occurred within the wood cell walls and not merely on the exposed surface or cell lumen. This result was confirmed by SEM-EDX analysis.

The high signal to noise ratio in Figure 2c indicates that, most of the x-ray signals displayed in the silicon mapping can be attributed to the IPTES in the modified specimen. In Figure 2a and 2b, the intermediate zone of W-IPTES is displayed and reveals that earlywood was more loaded with silane than latewood: lower signal intensities are actually detected in latewood, especially in the primary wall and middle lamella region. Such distribution may be attributed to the incomplete diffusion of IPTES in the thicker latewood cells (approx. 4-8 μm), compared with early wood cells (2-4 μm). The lumen of IPTES modified cells stayed empty, indicating that carbamoylation occurred within the wood cell walls only, where the reactive hydroxyl groups can be found.

W-IPTES was characterised by FTIR and solid state NMR spectroscopy. Both sawdust and wood blocks were analysed after treatment but only the results obtained with highly modified sawdust are presented (WPG = 138.5%).

In Figure 3, the characteristic FTIR vibrations of the carbamate function of W-IPTES emerged at 1718 cm^{-1} ($\nu_{\text{C=O}}$), 1542 cm^{-1} ($\delta_{\text{N-H}}$) and $1210\text{-}1310\text{ cm}^{-1}$ ($\nu_{\text{C-O}}$ and $\nu_{\text{C-N}}$). In addition, characteristic triethoxysilyl vibrations were identified at 957 cm^{-1} (Si-O-Et), $830\text{-}730\text{ cm}^{-1}$ ($\nu_{\text{Si-C}}$ and/or $\nu_{\text{Si-O}}$), and at $500\text{-}415\text{ cm}^{-1}$ ($\delta_{\text{O-Si-O}}$). Bands at 2972 and 2929 cm^{-1} were assigned to C-H stretching vibrations of the grafted groups.

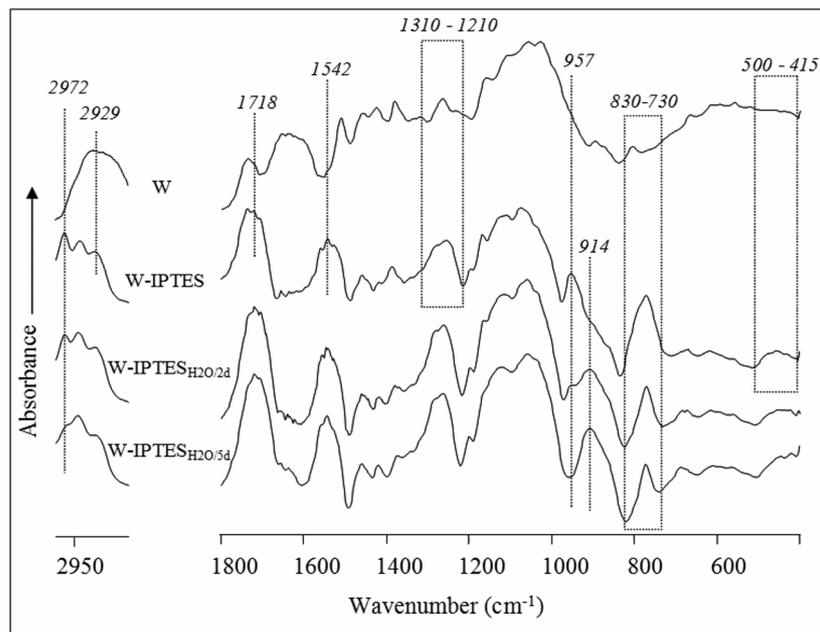


Figure 2: FTIR spectra of unmodified (W) and carbamoylated sawdust (W-IPTES). Spectra obtained after 2 and 5 days immersion in water are also presented (W-IPTES_{H₂O/2d} and W-IPTES_{H₂O/5d} respectively).

The grafting was also confirmed by CP-MAS ¹³C NMR analysis in Figure 3. Signals of the grafted groups were assigned according to the nomenclature displayed in Figure 1: *i.e.* 13 ppm (c), 21 ppm (a), 26 ppm (d), 46 ppm (e), 61 ppm (b) and 160 ppm (f).

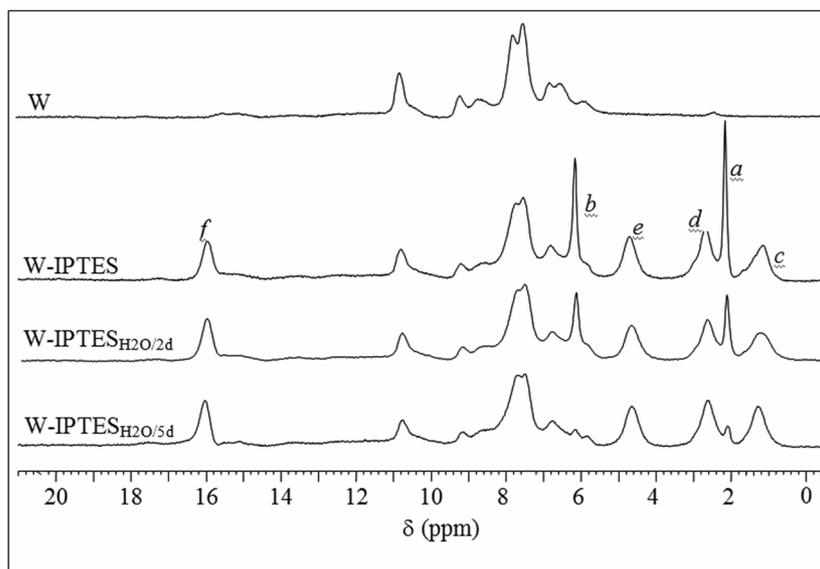


Figure 3: CP-MAS ¹³C NMR spectra of unmodified (W) and carbamoylated sawdust (W-IPTES). Spectra obtained after 2 and 5 days immersion in water are also presented (W-IPTES_{H₂O/2d} and W-IPTES_{H₂O/5d} respectively).

Hydrolysis of carbamoylated wood

To study the reactivity of the grafted triethoxysilane groups in wood, the hydrolysis of these moieties was performed (Figure 1B) and the modifications characterised by FT-IR and solid state NMR spectroscopy. Accordingly, W-IPTES sawdust (WPG = 138.5 %) was immersed in water

for 2 and 5 days and the FTIR spectra recorded (Figure 2). After prolonged contact with water, a strong band emerged at 914 cm^{-1} and was assigned to Si-OH stretching vibrations formed after hydrolysis of Si-OEt bonds (Cai *et al.* 2000). At the same time, vibrations associated to the ethoxy group at 957 cm^{-1} , 2972 cm^{-1} and $730\text{-}830\text{ cm}^{-1}$ decreased. Confirmation of this result is given by CP-MAS ^{13}C NMR analysis in Figure 3. After two, then five days contact with water, a decrease in the intensity of *a* and *b* type carbons is noted, which demonstrates clearly that a cleavage of Si-OEt bonds occurred, as expected. This hydrolysis reaction is however slow since Si-OEt cleavage is only partial after two days in water and is still not completely achieved after five days.

The reactivity and structure of the grafted alkoxy silane ends were further determined by ^{29}Si CP-MAS NMR spectroscopy (Figure 4). The chemical shift of ^{29}Si is sensitive to its local electronic environment *i.e.* condensation of Si-OR into Si-O-Si linkage results in an upfield shift of about 8-9 ppm for the silicon, whilst hydrolysis of the Si-OR linkage to Si-OH results in a downfield shift of 1-2 ppm (Douskey *et al.* 2002). After carbamoylation (W-IPTES), a dominant environment was found for silicon at -50 ppm and was assigned to $-\text{Si}(\text{OEt})_3$ ends of Figure 1A. The two additional signals at -57 and -63 ppm were assigned to the formation of a number of Si(OSi) and Si(OSi) $_2$ sites, through condensation reactions between neighbouring SiOEt groups. After five days in water (W-IPTES $_{\text{H}_2\text{O}/5\text{d}}$), new chemical shifts were observed at about -43, -53, -62 and -71 ppm and are assigned in figure 4. The relative intensities of the signals in W-IPTES $_{\text{H}_2\text{O}/5\text{d}}$ reveal that mono and di-condensed structures are mostly found in wood after prolonged contact with water. This result can be easily explained by the high WPG of the sawdust used for this study (WPG = 138.5%), the condensation of neighbouring SiOH groups in wood being highly favoured in that case.

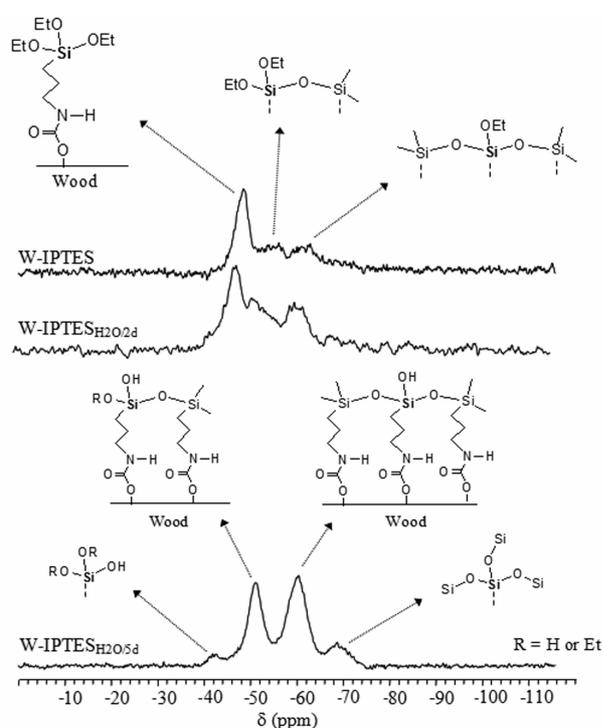


Figure 4: CP-MAS ^{29}Si NMR spectra of carbamoylated sawdust before hydrolysis (W-IPTES) and after 2 and 5 days immersion in water (W-IPTES $_{\text{H}_2\text{O}/2\text{d}}$ and W-IPTES $_{\text{H}_2\text{O}/5\text{d}}$ respectively).

CONCLUSIONS

The objective of the current paper was to fully investigate the chemical grafting of triethoxysilane end groups in wood *via* carbamoylation with IPTES and to study the reactivity of the grafted groups with regard to subsequent hydrolysis. The combination of analytical techniques (WPG, SEM-EDX, FTIR, solid state NMR) proved that carbamoylation occurred as expected and that the grafts were located within the wood cell walls. The presence of $-\text{Si}(\text{OEt})_3$ end groups in the solid matrix was confirmed, though a small number of self-condensed structures were also detected. The formation of silanol groups after hydrolysis of highly-carbamoylated wood was evidenced by infrared spectroscopy but CP-MAS ^{29}Si NMR analysis indicated that most of the silicon structures in the samples studied (high WPG) were in a mono- or di-condensed form. It is believed that the grafted silanol moieties could be used as anchoring sites for the further fixation of SiOH-terminated compounds (such as silicones). Therefore, the condensation of neighbouring silanol structures in wood has to be avoided and the WPG after carbamoylation has to be accordingly optimised.

ACKNOWLEDGEMENTS

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ASPECTS OF WOOD MODIFICATION WITH SILICON COMPOUNDS: MATERIAL PROPERTIES AND PROCESS DEVELOPMENT

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Keywords: Silane, sol-gel-process, hydrophobation, SEM-EDX, penetration, basidiomycete resistance

ABSTRACT

Two different impregnation methods of silane systems were compared with regard to penetration into the cell wall and the resulting wood properties. SEM-EDX mapping of silicon showed that treatment with monomeric silanes (wood was conditioned to fibre saturation) caused a high degree of cell wall penetration. In contrast, treatment with pre-condensed sols resulted in deposition of silicon mainly in the lumina. Incorporation of silicon in the cell wall caused a stronger improvement of wood properties such as dimensional stability, reduced moisture sorption or fungal resistance than deposition in the lumina. However, these improvements decreased after a longer storing time, due to ageing of the gels within the cell wall. HS 2909, a waterborne silane oligomer from alkyl and amino silanes and F 8815, an aqueous modified fluoroalkylsiloxane brought about high liquid water repellence, while EMC and dimensional stability were not changed by the treatment. These oligomers imparted wood with resistance against white and brown rot decay. Decay resistance was also caused by another two oligomeric silane systems which contain amino groups.

INTRODUCTION

Silanes used for treatment of solid wood bear three or four alkoxy groups. These can be hydrolysed to form silanols which subsequently condense to three-dimensional units. Condensation already starts while the hydrolysis is still in process, leading first to the formation of colloidal oligomeric particles called sols. Further reaction causes cross-linking of these sol particles, so that highly condensed gels are formed (sol-gel-process; Mai and Militz 2004a, b).

Different strategies to apply alkoxy silanes on wood have been described in the literature using the sol gel process to incorporate silica gels in wood. In one process, the bound and free water in the wood was used to initiate the hydrolysis of the alkoxy silane, in order to conduct the sol-gel process within the wood cell wall (Saka *et al.* 1992, Ogiso and Saka 1993). In another approach, silanes were hydrolysed in a batch before impregnating wood (Donath *et al.* 2004, Mai and Militz 2004a).

Silane treatment improved dimensional stability, water repellence and showed the ability to protect preservatives against leaching. Organofunctional trimethoxysilanes applied in combination with fire-resisting or antifungal agents and gel forming precursors such as TEOS have been shown as having synergistic effects. Systems containing several boron and phosphorous based agents enhanced the fire resistance of wood, which could be maintained after a leaching procedure with water, due to the hydrophobicity of the organo-functional silane (Saka and Tanno 1996, Saka and Ueno 1997). A quaternary ammonium

compound embedded in the sol-gel-process was capable to reduce decay of hinoki wood by the brown-rot fungus *Tyromyces palustris* and the white rot fungus *Trametes versicolor* (Tanno *et al.* 1998).

EXPERIMENTAL

Wood samples

Weight percent gain, anti-shrink efficiency and water repellent characteristics were determined using samples of steamed beech (*Fagus sylvatica*) with a size of 25 x 25 x 10 mm³ (rad x tang x long). Steamed beech (*Fagus sylvatica*) and Scots pine sapwood and heartwood (*Pinus sylvestris*) with a size of 5 x 10 x 30 mm³ were used to determine the decay resistance against basidiomycetes.

Chemicals

Monomeric silanes tested were tetraalkoxysilane (TEOS), methyltriethoxysilane (MTES) and propyltriethoxysilane (PTEO). Oligomeric silane systems which contain aminosilanes are presented in Table 1. Dynasylan® F 8815 is an aqueous fluoroalkylsiloxane. Specifications for silane concentrations were referred to the proportion of silane used in the synthesis mixture. For example the silane concentration in HS 2909 is 3.01 mol l⁻¹ (equivalent to 60 weight % solution of active compound in water).

Table 1: Oligomeric silane systems containing aminosilanes

Chemical name	Trade name	Condition	Amine type	Alkyl groups at amine	Additional alkyl groups
Amino-alkyl-functional oligomeric siloxane	DYNASYLAN® HS 2909	Acid	Primary	C ₃ H ₆	C ₄ H ₉
Aqueous 3-aminopropylsilane hydrolysate	DYNASYLAN® 1151	Alkaline	Primary	C ₃ H ₆	
Modified aminoalkylsilane hydrolysate	DYNASYLAN® 1154	Acid	Primary	C ₃ H ₆	

Treatment of wood specimens

The silanes TEOS, MTES and PTEO were used in two different states (Donath *et al.* 2004):

1. Silane state: Ethanol (1 mol), which was acidified with hydrochloric acid (37%) was added to 1 mol silane and stirred at ambient temperature for 30 minutes.
2. Sol state: Acidified (HCl, 37%) water (2.5 mol) was mixed with 1 mol silane and ethanol (1 wt %) as a solvent mediator. The mixture was stirred at room temperature until it became transparent and kept without stirring for 1 hour. When prepared in this way, the solutions stayed stable for several hours to a few days if the alcohol was allowed to evaporate, however, if the solution was covered, a longer pot life was observed.

The aqueous functional silanes HS 2909, DS 1151, DS 1154 and F 8815 were diluted with tap water to several concentrations with respect to the specific aims of the experiments.

The weight percent gain (WPG) was determined as previously described (Donath *et al.* 2004). All silanes were supplied by Degussa AG, Rheinfelden, Germany.

Moisture related properties

Sorption behaviour and dimensional stabilisation were determined as described in Donath *et al.* (2004). The water repellent characteristics were determined by submersing the samples in tap water. After given times the samples were removed from the water batch, dabbed off with tissue and weighed. The relative water uptake (WUR) and the water repellent effectiveness (WRE) was calculated according to the following equations (n = 10):

$$WUR = \frac{m_{\text{submersed}} - m_{\text{conditioned}}}{m_{\text{dry;untreated}}} \cdot 100\% \quad WRE = \frac{WUR_{\text{treated}} - WUR_{\text{untreated}}}{WUR_{\text{untreated}}} \cdot 100\%$$

Durability

Resistance against the white-rot fungus *Trametes versicolor* and the brown-rot fungus *Coniophora puteana* was determined in a mini-block test (Bravery 1978) following EN 113 (Donath *et al.* 2004).

Distribution of silicon in the wood cells

Cross sections of treated beech wood were prepared with a thickness of 10µm and then carbon coated. SEM micrographs of these slices were generated with a Hitachi S 2300 scanning electron microscope at an accelerating voltage of 15 kV. EDX measurements were performed with a Röntec X-flash detector at a band width of 1.710-1.856 keV to obtain Si-mappings of the cuts.

Long-term stability during pilot plant impregnation

Repeated impregnations were performed in a 750 litre vessel using HS 2909 solution with an active ingredient concentration of 10 %. Initially, the concentration of the silane solution was 10 % and then, for the last two treatments, raised to 15 %. After each impregnation, the remaining solution was collected and re-used in the next impregnation. New prepared silane solution was added if necessary. Treatments were performed on pine boards (sapwood and heartwood) with a size of 30 x 80...100 x 1400 mm³. Impregnation was carried out by a vacuum-pressure process (30 min 100 mbar, 2 h 11 bar). A total of 10 impregnations were performed over a time period of 16 weeks.

RESULTS AND DISCUSSION

Silane uptake

The aim of the first set of experiments was to study the effect of the silane state during the impregnation of the wood samples. Both treatment procedures were based on the sol-gel process. However, in one procedure, the silanes were hydrolysed and pre-condensed before treatment and impregnated as sols, in the other procedure, wood was impregnated with monomeric silane, in which it was intended to use cell wall-bound water for hydrolysis and condensation within the cell wall.

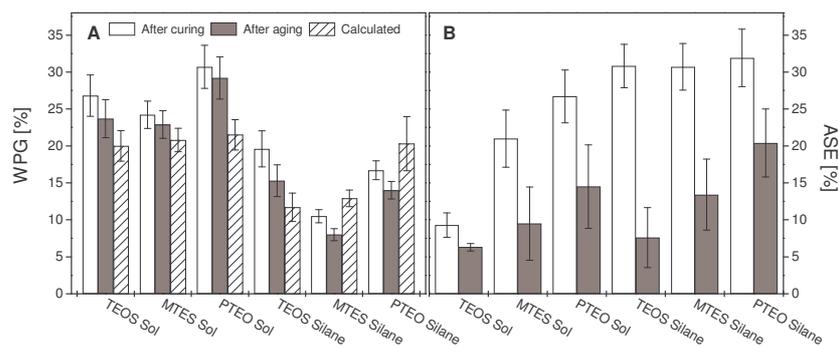


Figure 1: Weight percent gain (WPG) and anti swelling efficiency (ASE) of beech wood due to modification with alkoxysilanes; the „calculated“-values are determined by the uptake of impregnation solution

The weight percent gain (WPG) of the wood samples after treatment was dependent on the treatment procedure applied (Fig. 1A). Those samples that were impregnated with pre-hydrolysed silanes, here referred to as sols, displayed a higher WPG than pre-conditioned specimens which were treated with monomeric silanes. A theoretical WPG was calculated for each sample based on the uptake of the impregnation solution after the vacuum-pressure impregnation step. For this calculation, complete hydrolysis of the alkoxy groups in the silanes and condensation of all silanol groups was assumed. The WPG of all samples treated with sols were higher than calculated. This can be explained by incomplete hydrolysis and condensation.

The WPG diminished after storing of the samples in different relative humidity conditions and subsequent drying steps, which were performed in order to determine the equilibrium moisture content (EMC). The reduction in weight can be explained by an ageing process. Obviously, the silicon dioxide network within the wood was not fully condensed after the first curing. Further hydrolysis and condensation caused a cleavage of ethoxy and water molecules which resulted in a reduction in weight and WPG.

Water related properties

The EMC at various ambient humidity conditions was slightly reduced by all treatments compared to an untreated control, while it was higher in the samples treated with TEOS sol. All silane treatments resulted in lower moisture uptake than the corresponding sol treatments. After ageing, the EMC of all treated samples diminished considerably and was almost as high as in the untreated samples (not shown).

All silane treatments caused anti swelling efficiencies (ASE) of about 30 %, while the ASE of the sol treated samples was dependent on the type of silane used (Fig. 1B). Among the sol treated specimens, the ASE was low with TEOS (9 %), but it was significantly higher in the samples treated with the alkyl silane MTES (21 %) and PTEO (27 %). Generally, sol treatment showed lower dimensional stabilisation than treatment with monomeric silane.

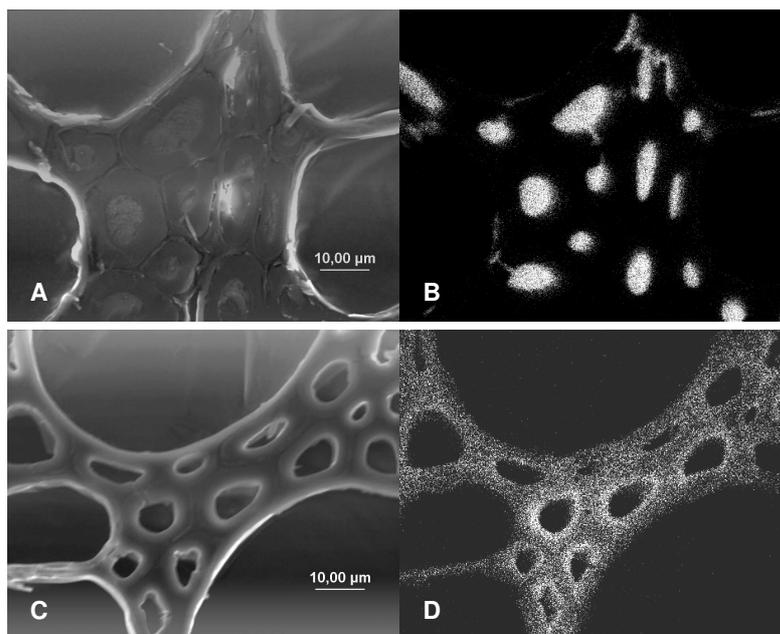


Figure 2: A, C: SEM micrographs of beech wood specimens treated with MTES (1500x; cross sections); B, D: the corresponding SEM-EDX mappings of silicon in beech. A, B: Treatment with pre-hydrolysed MTES (sol state); C, D: Treatment with monomeric MTES (silane state)

Higher values of ASE in samples treated with monomeric silanes corresponded with a higher cell wall bulking compared to sol treatment. These differences are caused by a better penetration of monomeric silanes into the cell wall than the sol particles that possess a much higher particle size. In addition, monomeric silanes were dissolved in ethanol, while sols were applied without a solvent. Ethanol swells the cell wall and opens the micropores, allowing silane molecules to penetrate. SEM-EDX studies revealed a higher deposition of silicon in the cell wall of wood treated with monomeric silane (Fig. 2).

Treatments with silanes considerably diminished the water uptake of small wood samples in the initial submersion phase of 4 hours (Fig. 3). The presence of hydrophobic alkyl groups was required for a water repellent effect in the case of treatment with alkoxy silanes in the sol state. Thus, pre-condensed TEOS (sol) did not impart water repellent properties to wood, while monomeric TEOS did. This result can be explained with the high deposition of silicates in the cell wall, when applied in the silane state.

All monomeric silanes and the multifunctional water borne silane systems HS 2909 and F 8815 caused a reduced water uptake, independently from the organo-functional groups. After a longer submersion time (24 h), the hydrophobic effect lessened, whereas the best long term stability was shown by multifunctional water borne silane systems. Reduction in concentration of HS 2909 did not result in reduced hydrophobicity. Considering the applied concentration of silanes as well as the weight gains, the highest effectiveness could be reached by the aqueous silane systems (Fig. 3).

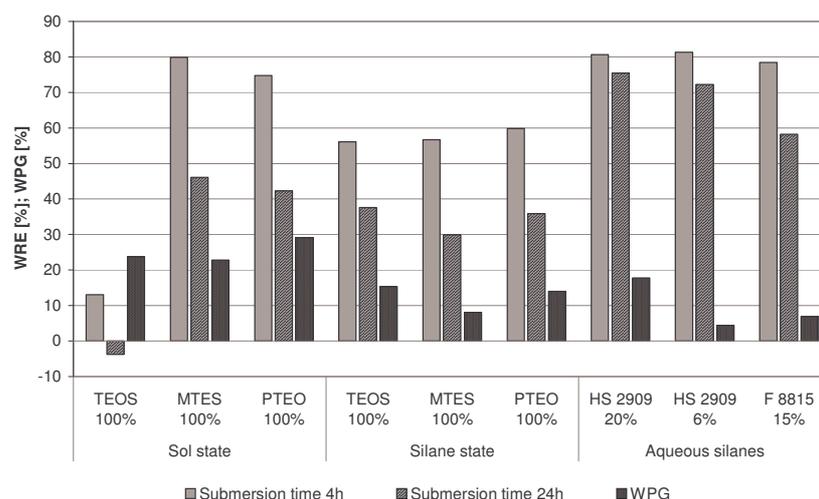


Figure 3: Reduction of water uptake in submersion test performed with small samples (high portion of cross-sections at wetted surface). High water repellent efficiency (WRE) means low water uptake.

Resistance against decay fungi

Beech wood specimens treated with monomeric silanes and pre-condensed sols were tested for their resistance against the white rot fungus *Trametes versicolor* in a mini-block test (Bravery 1978). All treated samples displayed a reduction of decay with the exception of those treated with the sol of TEOS (Table 2). As a tendency, the treatment of fibre saturated wood with monomeric silanes caused a higher durability than the treatment with pre-condensed sols. The lowest weight loss was observed with samples treated with MTES and PTEO (silane treatment). According to the European standard EN 350, these samples are classified as very durable (class 1). The corresponding sol treatments led to durability class 2 (PTEO) and class 3 (MTES). With respect to the treatment method, the highest difference in durability was observed with TEOS. As shown above, a treatment with monomeric silanes caused the incorporation of higher amounts of silicon compounds into the cell wall. Obviously, this deposition of the silicon gels in the cell wall is crucial to cause effective protection.

Table 2: Mass loss of beech wood after 6 weeks exposure to *Trametes versicolor*

	WPG (%)	Mass loss (%)	x-value
Control		38.0	
TEOS sol 50%	12.6	37.0	0.97
MTES sol 50%	12.9	14.0	0.37
PTEO sol 50%	15.1	8.9	0.23
TEOS silane 100%	13.1	8.4	0.22
MTES silane 100%	11.0	5.2	0.14
PTEO silane 100%	14.1	5.1	0.13

In a further experiment, basidiomycete testing was performed with specimens treated with the multifunctional siloxane oligomer Dynasytan® HS 2909. This silane is a fully hydrolysed, water-soluble oligomer which contains amino- and alkyl-functional groups but also hydroxyl groups that can further condense.

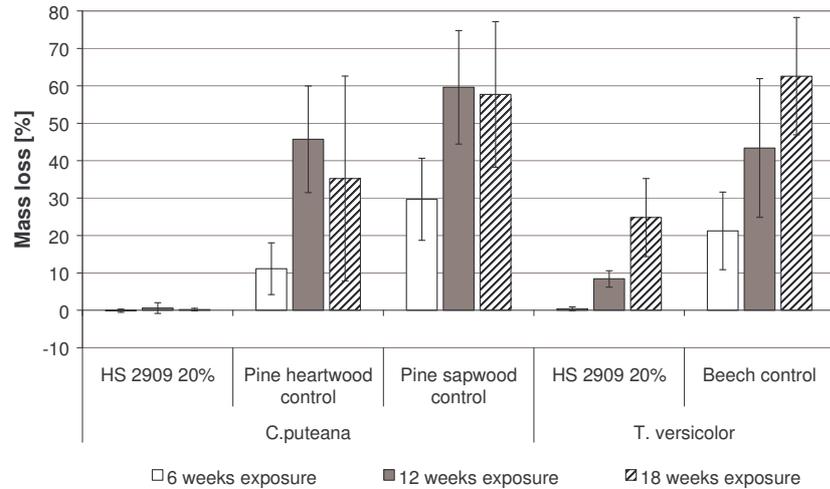


Figure 4: Mass loss of silane-treated pine sapwood and beech mini blocks after 6, 12 and 18 weeks exposure to *C. puteana* and *T. versicolor*, respectively

The weight loss caused by fungi depends on the time the fungus needs to colonise the wood and on the decay rate required to mineralise the cell wall. Wood blocks treated with conventional biocide preservatives are normally not colonised by the test fungus. When wood is treated with water repellents, the colonisation can be decelerated, because the water content is initially too low to allow fungal growth. However, when the fungus has once established in the wood, the decay rate is often as high as in untreated samples. The influence of a lag in colonisation is very high, when mini-blocks are used as test specimens (Bravery 1978), since the test period is short. For that reason, fungal tests were run over 6, 12 and 18 weeks.

HS 2909 was more efficient in preventing decay by the brown-rot fungus *C. puteana* than by the white-rot fungus *T. versicolor*. The WPG of the pine samples treated with HS 2909 amounted to 16.2 %; that of beech samples to 10.9 %. Treated pine wood was fully protected against *C. puteana* over the whole exposure time of 18 weeks. In contrast, treated beech wood resisted decay by *T. versicolor* only during the first 6 weeks of exposure. Decay by *T. versicolor* occurred after 12 weeks incubation time of HS 2909 treated samples, but at a low rate (Fig. 4).

The rate of decay of wood can be accelerated by reducing the mass of individual wood specimens. Toxic values obtained with mini-blocks after 6 weeks incubation period compared well with those obtained after 12 weeks using sample sizes described in EN 113 (Bravery 1978). Thus, 12 and 18 month incubation in a mini-block test is a more severe decay condition than that described in EN 113 and shows the effectiveness of this multifunctional silane.

A comparison of alkylsilanes and HS 2909 showed that the oligomeric silane system caused a higher reduction in the decay rate at similar WPG values. This may be attributed to the amino groups in the oligomer. Two oligomers of aminopropyl triethoxy silane were compared to HS 2909, in order to study the effect of amino groups. These silanes were used with two concentrations. High concentrations

are related to the SiO-fraction, low concentrations are related to the amino-fraction of the 20% solution of HS 2909 (see Table 3).

Table 3: Weight gain and mass loss of pine sapwood mini blocks after 12 weeks exposure to *C. puteana* and moisture content of samples stored above agar. Standard deviations are displayed in parentheses.

Treatment	WPG [%]	Mass loss [%]	Moisture content above agar [%]
HS 2909 20%	18.4 (1.7)	-2.7 (1.9)	46.2 (2.6)
DS 1151 22%	18.7 (1.8)	7.9 (1.4)	116.6 (1.6)
DS 1151 11%	10.9 (1.1)	4.1 (0.4)	115.3 (10.2)
DS 1154 23%	22.0 (2.0)	0.9 (1.8)	87.9 (3.1)
DS 1154 13%	13.1 (1.1)	0.8 (1.2)	72.4 (1.9)
Control		63.1 (8.2)	32.7 (2.1)

All samples except those treated with DS 1151 displayed a weight loss lower than 1 % after 12 weeks incubation with *C. puteana*. Samples treated with the alkaline solution of DS 1151 lost 4.1 and 7.9 % of its initial weight (Table 4). Amino silanes applied in acidic solutions contain ammonium groups which can affect fungal physiology in a way comparable to quaternary ammonium compounds. In alkaline solutions of DS 1151 the amino groups are not protonated (cationic) so that there is a minor effect.

A concentration of 20 % HS 2909 was necessary to impart full resistance against *C. puteana* to pine wood. DS 1154 imparted comparable protection at lower concentration, most probably due to the same concentration of amino groups in the formulation. These results show that high decay resistance is caused mainly by cationic amino groups and the hydrophobic alkyl groups, which are only present in HS 2909, exert a minor effect on decay resistance.

Long-term stability during pilot plant impregnation

Silanes are known as “living” systems. Hydrolysis, condensation and network forming occur at the same time, when silanes are once in contact with water. Pre-hydrolysis, as it was described in the first experiment is not feasible in practice, since it leads to gelation of the impregnation solution within a short time (several hours up to few days).

HS 2909 is a multifunctional silane co-oligomer. During the synthesis, the alcohol formed by hydrolysis of ethoxy groups was substituted by water. These water-soluble, alcohol-free oligomers contain amino- and alkyl-functional groups but also silanol groups which can further condense.

A solution of this oligomer was used to impregnate wood boards in a pilot plant. Between the impregnation processes, the silane solution was stored in dark plastic barrels at temperatures of 18-25°C. Overall, conditions can be described as comparable to a well-managed impregnation plant.

Visual observations revealed an almost constant appearance of the treatment solution. A light yellowing was presumably caused by leaching of wood extractives. Viscosity remained comparable to water; even at a check three months after the last impregnation (19 months in

total), no changes were observed. Filtering with a 40 µm filter revealed no residues. Measurements of solids content and pH-value revealed high stability over the whole project duration (16 weeks).

It can thus be concluded that the silane was not affected by the stresses of impregnation procedures including the contacts with metals, plastic, wood, moisture and air. The high stability may be caused by the special synthesis procedure of the stock solution. The described observations have revealed the suitability of the special silane formulation HS 2909 for the use in regularly operating impregnation plants.

CONCLUSIONS

Impregnation of wood with pre-condensed sols did not significantly improve wood properties such as EMC, dimensional stability or fungal resistance. This failure can be explained due to minor deposition of siloxane in the cell wall. SEM-EDX mapping of silicon showed that higher amounts of siloxanes could be incorporated into the cell wall when wood was conditioned to fibre saturation and subsequently treated with monomeric silanes. This treatment procedure resulted in improved wood properties but these were not stable due to aging of the gel formed in the cell wall. In addition, the procedure is hardly feasible in practice, because wood must be conditioned to fibre saturation and the silane must be applied in a water-free solvent.

Water-borne silane oligomers such as HS 2909 and F 8815 can be diluted with water and directly applied for impregnation. These systems impart high liquid water repellence and fungal resistance, but did not change EMC and dimensional stability. High water repellence seems to be caused by the hydrophobicity of alkyl and fluoroalkyl groups combined with a good adhesion of polar amino groups to the cell wall polymers which enables a strong interaction of the siloxane and the cell wall.

Oligomeric silane system imparted wood with resistance against white and brown rot decay. This decay resistance seems to be based on the presence of cationised amino *i.e.* quaternary ammonium groups.

The water-borne silane oligomers HS 2909 and F 8815 showed high potential for the application on wood in use-class III (EN 335), due to their excellent water repellence and fungal resistance. In pilot plant experiments, the impregnation solution of HS 2909 (20 %) proved to be stable over 4 month and did not show any significant change in viscosity.

ACKNOWLEDGEMENTS

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STANDARD TESTING OF ORGANOSILICON COMPOUNDS AS WOOD MODIFICATION AGENTS

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Keywords: Hydrophobicity, organosilicon compounds, silanes, siloxanes, wood modification

ABSTRACT

Wood modification is a generalised term for treatments with the aim to enhance wood properties. It is important that no toxic residues are present in order to make it easy to dispose or recycle the wood at end of life. The most important properties to improve are dimensional stability, hydrophobicity, resistance to wood deterioration, fire retardance, mechanical properties and appearance of the wood. A group of chemicals which are considered suitable are the silanes and/or siloxanes. This study is part of a European Research Project with acronym HYDROPHOB with the objective to review the potential of silicon-based hydrophobisation agents as wood protection agents. Herein, dimensional stability and wood deterioration are main evaluation criteria. To get a general insight, both water and solvent based silanes and/or siloxanes are used. The starting point was a 1 % active ingredient concentration of the pure product, mainly for economic reasons. Different treatment procedures were set up, but at the end, the conclusion for all products and treatments was not very positive. Silanes and/or siloxanes, at the concentrations indicated, did not show any significant contribution to the biological durability when using laboratory fungal tests equivalent to efficacy testing of wood preservatives. Furthermore, no indication was found on increased dimensional stability induced by a chemical modification reaction.

INTRODUCTION

Wood is an important building material which can maintain its position due to its excellent properties and aesthetic appeal (Jones *et al.* 2003). Nevertheless, it is frequently treated in order to enhance these properties. Chemical modification of wood should result in an improvement of its biological and technical properties (Goethals *et al.* 1994). Organosilicon compounds and more specifically silanes and/or siloxanes have already been studied as chemical wood modifiers (Donath *et al.* 2004, Hill *et al.* 2004, Mai *et al.* 2003, Ritschkoff *et al.* 2003, Sèbe *et al.* 2001, Goethals *et al.* 1994, Belyj *et al.* 1985). They are also frequently used as a water repellent product for natural building stones (Cnudde *et al.* 2004) or as modification agents in the plastics, textile, building and paper industries (Donath *et al.* 2004).

The purpose of this paper is not to prove that one single siloxane does or does not work as a wood modification agent, but rather to show the potential of siloxanes as a group of chemicals for wood modification. This potential should not be based solely on the activity of the chemicals, but also reflect commercially feasible end products.

EXPERIMENTAL

Chemicals

Organosilicon compounds can be applied as impregnating or priming agents on wood. In the past, organic solvents were used to disperse these compounds, but for legislative and environmental reasons, nowadays waterborne products are preferred. Wood modification with silanes, and more specific alkoxy silanes has been reported before (Mai *et al.* 2004a, Mai *et al.* 2004b, Hill *et al.* 2004, Hager 1995). Polymerisation of the organo alkoxy silane monomer can be achieved either by free-radical polymerisation (if the attached organic moiety contains a reactive group), or via silanol condensation (Figure 1) to form siloxane bonds after hydrolysis of the attached alkoxy groups (Hill *et al.* 2004).

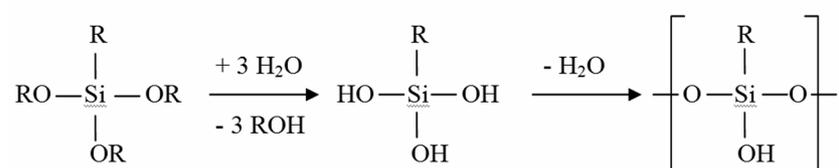


Figure 1: Formation of a siloxane

The use of silicone microemulsions is another option for water soluble organosilicon compounds. The microemulsions consist of an oil phase, a water phase, an emulsifier and a coemulsifier. These last two can be regarded as active ingredients (hydrophobing agents) at the same time. From the moment the concentrated microemulsions are poured into water, reaction takes place in the droplets. After activation, the silicone microemulsions gradually lose their effectiveness (Mai *et al.* 2004a, Hager 1995). In this paper, mixtures of octyltriethoxysilane (OTEOS), methyltrimethoxysilane (MTMOS) and polydimethylsiloxanes (PDMS) are used (Figure 2). Most products are a mixture of silanes and siloxanes and are further referred to as siloxanes. Table 1 gives an overview of the products used. Products A, B and C are emulsions, whereas product D is a microemulsion.

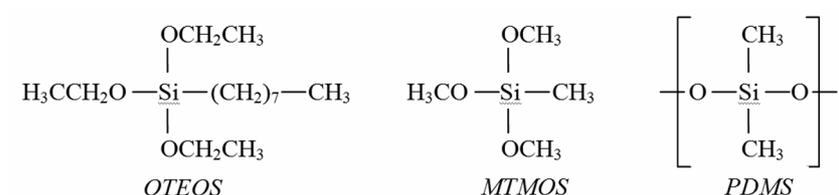


Figure 2: Chemical structure of the main components

Table 1: Product information

Product	Type	Solvent	Active ingredient concentrations (conc _{ai} , %w/w)					
A	PDMS	Aqueous	1%	5%				60%
B	OTEOS/DMS	Aqueous	1%	5%	10%	20%	30%	50%
C	DMS/OTEOS	Aqueous	1%	5%	10%	20%	30%	40%
D	PDMS/TEOS	Aqueous		5%	10%	25%	50%	100%
E	OTEOS	Isopropylalcohol		5.5%	11%	27%	53%	100%
F	MTMOS/OTEOS	Isopropylalcohol		6%	12%	29%	55%	100%

Treatment of specimens

Scots pine sapwood and beech specimens were impregnated with siloxane solutions. They were first conditioned in a climatic chamber (20°C, 65 % relative humidity (RH)) until they reached an equilibrium moisture content of about 12 %. Depending on the experiment, the specimens were impregnated with different active ingredient concentrations of products, as given in Table 1. The utmost right column indicates the highest concentration in the commercially available products (% w/w). The mass of each specimen prior ($m_{untreated}$) and after treatment ($m_{treated}$) was recorded and the weight percent gain (WPG) based on solution uptake calculated according to equation 1.

$$WPG(\%) = \frac{m_{treated} - m_{untreated}}{m_{untreated}} \times \text{conc}_{ai}(\%) \quad (1)$$

Dimensional stability

Dimensional stability was evaluated by means of both a water soaking and a vapour uptake test. Scots pine sapwood and beech specimens with dimensions 30 × 30 × 5 mm³ (radial × tangential × longitudinal) (Size 1) were vacuum impregnated with a 5 % concentration of products A, B or C.

The water uptake specimens (6 replicates) were dried under ambient conditions for 48 h and oven dried at 60°C for 24 h. Following mass and dimension measurements, specimens were leached with water including an impregnation step, all according to the European Standard EN84. Upon measurement of specimen dimensions and weighing, the samples were air dried and oven dried (60°C). The water impregnation/drying cycle was repeated three times. Three anti swell efficiencies (ASE) and anti shrink efficiencies (AsE) were calculated by comparing the volumetric swelling/shrinkage of the treated ($S_{treated}$) and untreated ($S_{untreated}$) specimens (Eqn. 2).

$$ASE(\%) = \frac{S_{untreated} - S_{treated}}{S_{untreated}} \times 100 \quad (2)$$

Three different drying/curing regimes after impregnation were evaluated with the vapour uptake specimens. The first regime was air drying, the second one drying for 24 h at 40°C and the third one drying for 24 h at 60°C. After this curing process, the specimens were conditioned until constant mass (20°C and 60 % RH) and then at constant temperature (20°C) subjected to changing RH. Starting from 60 % RH, this was increased up to 90 % RH and then back again to 60 % RH. This cycle was repeated three times. Three consecutive anti shrink and anti swell efficiencies could be determined (Eqn. 2).

Decay resistance

To have a first glance on the potential of siloxanes on protecting wood against Basidiomycetes deterioration, a first test was set up according to the European Standard EN 113 with siloxanes A, B and C. Both beech and Scots pine specimens (6 replicates) with dimensions $15 \times 25 \times 50 \text{ mm}^3$ (radial \times tangential \times longitudinal) (Size 2) were impregnated with a 1 % or 5 % concentration. They were incubated on malt agar overgrown with fungal mycelium in Kolle flasks for 16 weeks, as described in the standard. The brown-rot fungus *Coniophora puteana* was used for both beech and Scots pine, whereas the brown-rot fungus *Poria placenta* was only used on Scots pine sapwood and the white-rot fungus *Coriolus versicolor* on beech. Mass loss and moisture content of the specimens were determined at the end of the test.

To be able to screen more siloxanes, a second test was set up. To shorten the test period this time a miniaturised test, a so-called mini-block test with specimen dimensions $10 \times 5 \times 30 \text{ mm}^3$ (radial \times tangential \times longitudinal) (Size 3) was performed. Herein, 5 siloxanes (products B, C, D, E and F) were tested on beech and Scots pine sapwood in a concentration ranging from about 5 % active ingredient up to pure product (Table 1). One brown and one white rot fungus was used: *Coniophora puteana* on Scots pine and *Coriolus versicolor* on beech. Decay was evaluated by mass loss, as described in the European Standard EN113.

RESULTS AND DISCUSSION

Weight percent gain (WPG)

For both wood species, the WPG of water based products in a 5 % active ingredient concentration is on average 2 % higher than the equivalent of solvent based products (Figure 3). Scots pine has an average WPG for water based products between 4 % and 6 %, whereas WPG for beech was between 4 % and 4.5 %. The average WPG for the two solvent based products was 3 % and 2.5 % for Scots pine and beech respectively.

From the graphs in Figure 3, it can be concluded that the WPG for specimens of different sizes after impregnation with the same product at the same concentration is comparable, which makes it easier to have an overall discussion on these tests.

As is depicted in Figure 4, the WPG rises with increasing active ingredient concentration. More specifically, the WPG of solvent based siloxanes increased linearly with higher active ingredient concentration, whereas the WPG of water based products increased quadratically (R^2 above 97.46 % for Scots pine and above 98.69 % for beech).

Dimensional stability

The siloxane treatments did not alter the water uptake after impregnation of Scots pine sapwood and beech specimens with dimensions $30 \times 30 \times 5 \text{ mm}^3$ (radial \times tangential \times longitudinal). Both ASE and AsE of all cycles are close to zero (Figure 5).

Considering the vapour uptake specimens, no difference could be observed between the WPGs, ASE and AsE of specimens treated with the same products, but finished with a different curing regime. Only

Scots pine specimens impregnated with product A and cured for 24 h at 60°C had slightly higher ASE and AsE than specimens impregnated in the same way, but cured at lower temperatures. Because this difference was only small, all specimens treated with the same product were, regardless the curing regime, considered as one batch and analysed that way.

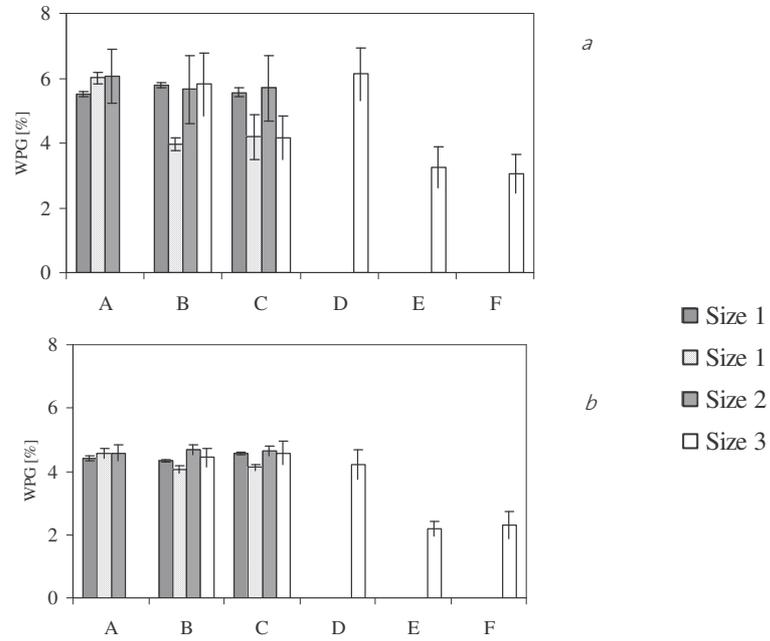


Figure 3: WPG of Scots pine sapwood (a) and beech (b) after impregnation with siloxanes at 5% active ingredient

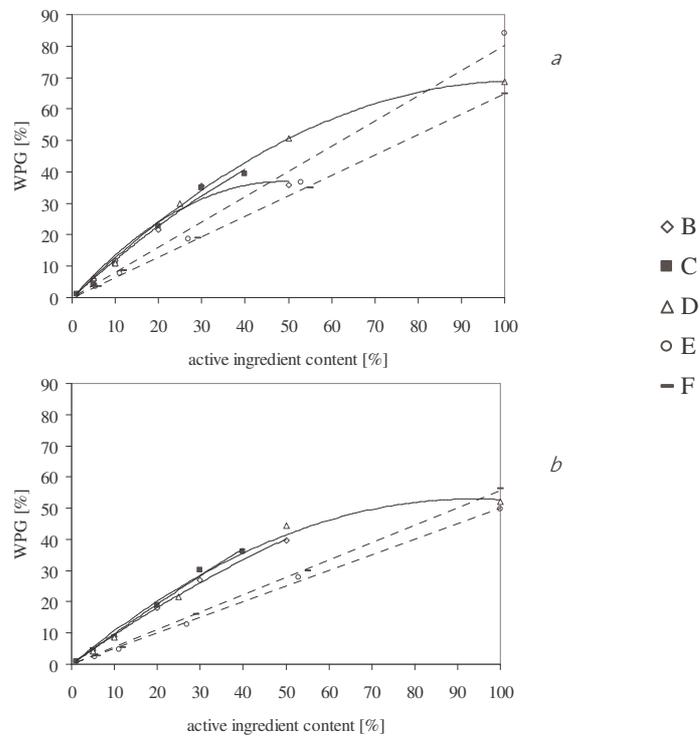


Figure 4: WPG of Scots pine sapwood (a) and beech (b) at different active ingredient concentrations

The vapour uptake of treated specimens was in some cases altered by the siloxane treatments (Figure 5). Scots pine specimens treated with products B and C showed a similar pattern during the cycles (Figure 5a). Specimens treated with product C revealed to a limited extent a lower swelling and shrinkage in the first cycle. In subsequent cycles, ASE and AsE became negative or zero, and the last AsE became positive again. Specimens treated with product B showed a similar pattern, but all efficiencies, except for the first ASE, were negative or zero.

The ASE and AsE of beech in the vapour uptake test was not influenced by the siloxane treatments, except for those treated with product A (Figure 5b). What's more, this last treatment gave the best results of all treatments, with ASE and AsE during all 3 cycles between 15 and 30 %. The graphs show for some products in the first cycle a positive effect of the treatments. Since this effect decreases from the second cycle on, the products do not seem to have a chemical bonding to the wood substances.

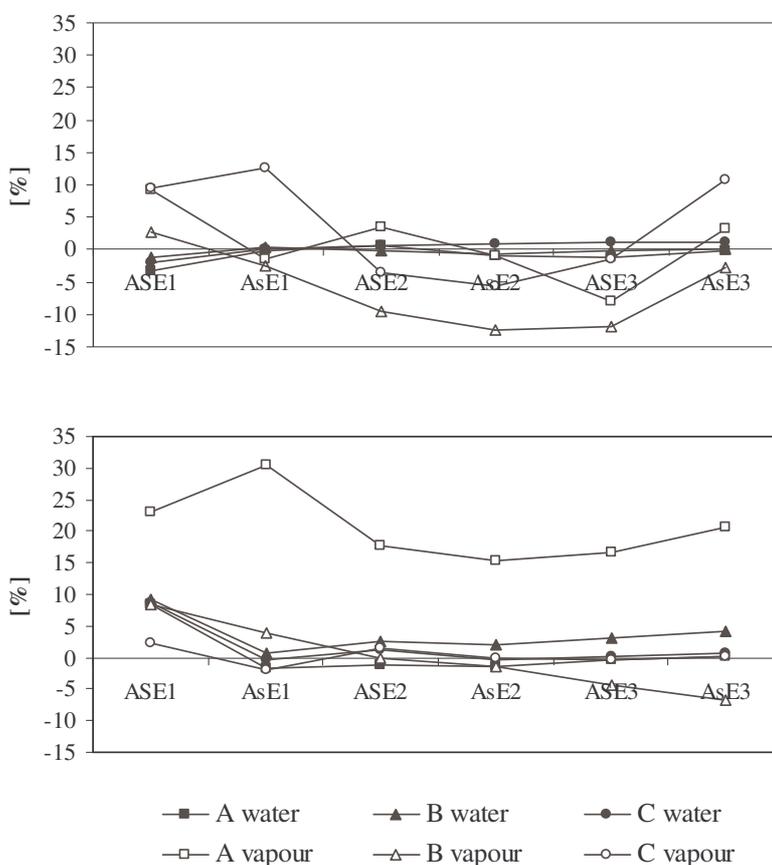


Figure 5: Anti swell (ASE) and anti shrink (AsE) efficiencies of Scots pine sapwood (a) and beech (b) treated with 3 siloxanes in a 5% active ingredient concentration during 3 consecutive cycles

Decay tests

No preservative effects of products A, B or C at concentrations 1 % and 5 % on Scots pine sapwood and beech could be detected after 16 weeks exposure to different fungi (Table 2 and Table 3). The mass losses indicated are calculated solely on the wood substance part of the

treated specimens and as such, are fully comparable to values recorded for untreated specimens.

Table 2: Average \pm standard deviation and median mass loss of wood substance of treated Scots pine specimens after 16 weeks exposure according to the EN113 test

	WPG [%]	Coniophora puteana		Poria placenta	
		Average [%]	Median [%]	Average [%]	Median [%]
A 1%	1.2	40 \pm 11	36	30 \pm 8	33
A 5%	6.0	40 \pm 8	34	31 \pm 2	26
B 1%	1.3	34 \pm 10	34	30 \pm 3	30
B 5%	5.7	45 \pm 8	49	29 \pm 3	29
C 1%	1.2	20 \pm 6	20	27 \pm 2	27
C 5%	5.7	20 \pm 5	19	30 \pm 7	31

Table 3: Average \pm standard deviation and median mass loss of wood substance of treated beech specimens after 16 weeks exposure according to the EN113 test

	WPG [%]	Coniophora puteana		Coriolus versicolor	
		Average [%]	Median [%]	Average [%]	Median [%]
A 1%	0.9	38 \pm 7	39	35 \pm 3	36
A 5%	4.6	44 \pm 5	43	40 \pm 2	40
B 1%	0.9	43 \pm 9	43	35 \pm 2	34
B 5%	4.7	49 \pm 7	48	37 \pm 3	37
C 1%	1.0	49 \pm 8	50	39 \pm 3	40
C 5%	4.6	42 \pm 12	42	Not determined	Not determined

Table 4: Average and median mass loss of Scots pine and beech specimens after 8 weeks exposure according to the mini-block test

	Scots pine Coniophora puteana			Beech Coriolus versicolor		
	WPG [%]	Average [%]	Median [%]	WPG [%]	Average [%]	Median [%]
B 5%	5.8	62 \pm 3	62	4.4	30 \pm 8	31
B 10%	12.0	53 \pm 11	56	8.8	37 \pm 6	37
B 20%	21.5	27 \pm 19	31	17.9	33 \pm 3	33
B 30%	35.4	10 \pm 5	9	26.9	26 \pm 14	25
B 50%	35.9	19 \pm 21	16	39.8	12 \pm 4	11
C 5%	-4.2	46 \pm 8	42	4.6	40 \pm 8	41
C 10%	10.7	47 \pm 3	47	8.5	40 \pm 7	40
C 20%	22.7	42 \pm 10	42	19.0	34 \pm 6	33
C 30%	34.9	33 \pm 11	32	30.2	-8 \pm 15	-6
C 40%	39.5	46 \pm 16	48	36.2	8 \pm 5	8
D 5%	6.1	23 \pm 20	24	4.2	29 \pm 1	29
D 10%	10.9	24 \pm 14	26	8.6	30 \pm 13	26
D 25%	30.0	0.5 \pm 5	1	21.6	15 \pm 3	15
D 50%	50.7	-7 \pm 5	-8	44.5	2 \pm 3	2
D 100%	68.7	-11 \pm 4	-11	52.2	9 \pm 4	10
E 5.5%	3.6	56 \pm 6	55	2.4	29 \pm 10	31
E 11%	7.7	53 \pm 5	54	4.9	31 \pm 6	31
E 27%	18.6	52 \pm 8	53	12.8	18 \pm 10	17
E 53%	36.8	34 \pm 15	40	27.8	15 \pm 3	14
E 100%	84.2	22 \pm 12	25	49.8	15 \pm 6	16
F 6%	3.6	30 \pm 29	32	2.8	29 \pm 4	25
F 12%	8.5	41 \pm 11	45	5.4	19 \pm 5	16
F 29%	19.0	-3 \pm 6	-8	15.9	10 \pm 7	10
F 55%	34.9	3 \pm 7	4	30.0	3 \pm 2	3
F 100%	64.9	-5 \pm 7	-5	56.3	12 \pm 11	8

Treated Scots pine and beech mini-block specimens exposed for 8 weeks to brown and white rot fungi on malt agar medium showed only low decay resistance (Table 4). In general it can be concluded that the higher the WPG was, the lower the mass loss of the treated specimens. Although this general observation is valid, a few treatments could give a protective efficacy based on the mass loss limit of 3 %. For Scots pine only, products D and F at active ingredient concentrations higher than 25 %, or a WPG above 30 % and 19 % respectively, resulted in a mass loss lower than 3 %. The mass loss of specimens treated with products A and B at low concentrations, was in some cases even higher than the mass loss of untreated specimens.

Beech could only be adequately protected by products C, D or F at WPGs higher than 30 %, 50 % and 55 % respectively.

DISCUSSION

Goethals *et al.* (1994) reported average ASE after 5 wet/dry cycles for Scots pine and beech after impregnation with propyltrimethoxysilane (PTMOS). At 12.5 % and 24.4 % weight gain, Scots pine had an ASE of 21 % and 27 %, respectively. Beech at 8.5 % and 11.5 % weight gain had ASE of 31 % and 35 % respectively. They claim the disappointing result of PTMOS to the fact that not all of the silanol groups present reacted with the hydroxyl groups of the wood constituents. Hill *et al.* (2004) found only moderate improvement (less than 40 % ASE) in dimensional stability of Corsican pine treated with [γ -(methacryloxy)propyl] trimethoxysilane (TMPS) or vinyltrimethoxysilane (VTMOS), even at WPGs up to 50 %. Schneider *et al.* (1985) on the other hand, found for white birch, trembling aspen and eastern white pine treated with TMPS that the ASE could amount up to 60-70 % at 25-40 % weight gain. Donath *et al.* (2004) treated beech with tetraethoxysilane (TES), propyltriethoxysilane (PTEOS) and methyltriethoxysilane (MTEOS) in two different treatments (monomeric silane and pre-hydrolysed sols). Although generally, monomeric silane showed higher dimensional stabilisation than a pre-hydrolysed sol treatment, at WPGs between 10 % and 30 % no ASE above 30 % was reported. The ASE decreased after ageing.

Silylation with PTMS did not contribute at all to a better decay resistance for beech (*Coriolus versicolor*) between 2.75 % and 14 % weight gain and for Scots pine (*Coniophora puteana*) between 3 % and 22 % weight gain (Goethals *et al.* 1994). Hill *et al.* (2004) also found only a small reduction in mass loss due to treatment of Corsican pine with VTMOS or TMPS exposed to *Coniophora puteana*, even at WPGs in excess of 45 %. Donath *et al.* (2004) reported a reduction of decay of beech by *Coriolus versicolor* between 5 % and 8 % mass loss and between 9 % and 37 % mass loss when treated with TES, PTEOS or MTEOS as monomeric silane or as pre-hydrolysed sol, respectively.

The results obtained in this paper confirm what has been found before: siloxanes at commercially feasible concentrations (*i.e.* approximately 5 % WPG) tested with standard laboratory tests fail to show improved dimensional stability or decay resistance. Strictly, they do not act as a chemical wood modifying agent inducing chemical stability.

Although not yet confirmed by raw data in this research, it was noticed that treated wood blocks (*e.g.* in field exposure) had lower crack

formation, better water repellency and lower wettability. During consecutive wet and dry periods, the wood mass didn't change as fast as those of untreated wood blocks. These observations make it reasonable to expect better performance of treated wood in practice, *i.e.* decking. This performance testing is however different to the wood preservative biocides approach evaluating efficacy (EN113, EN599) and/or ASE evaluation of dimensional stability.

CONCLUSIONS

A different approach for performance evaluation is needed when dealing with hydrophobic treatments. Standard wood preservative testing is only showing efficacy at very high concentrations for some products. A better approach could be to compare the products with a reference material of moderate durability, either treated or not. Considering dimensional stability, the methods linked to detecting chemical reactions are not able to qualify the performance of hydrophobic treatments using siloxanes. In general it can be concluded that laboratory testing of both decay resistance and dimensional stability need to be adopted for siloxane treatments. Anyhow, physical properties like wettability, crack formation and moisture relationship in general can be the dominant parameters in practice. Field testing alongside a more elaborate evaluation of the protective nature of siloxane treatments seems to be the only way to establish confident evaluation of these non-biocidal treatments.

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CHEMICAL MODIFICATION OF WOOD WITH SILICON COMPOUNDS

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Keywords: Decay test, dimensional stability, durability, field test, modified wood, silicon

ABSTRACT

The objectives of this study were to investigate the decay resistance of silica modified wood by laboratory and field testing. Modified pine samples were exposed to field testing for four years for above ground and two years for ground contact, according to standards ENV 12037 and EN 252 respectively, in Ultuna, Sweden. In addition, silica treated samples were tested for laboratory decay resistance and dimensional stability. The silica impregnated samples showed a durability similar to that of CCA impregnated controls in above ground standard lap-joint test. The durability of the stakes in ground contact was also improved, when compared to the untreated controls but four years of exposure is too short a time for conclusions.

INTRODUCTION

Wood is a renewable, economical and biological material that has made it one of the most commonly used construction materials. However, depending on the application, there are certain properties which restrict its use. In particular, these properties are related to its dimensional instability, a function of moisture content, biodegradability and flammability (Larsson 1993, Hon and Shiraishi 2001, Sèbe and Brook 2001). These negative properties can be improved by chemical modification of wood components. Various types of chemicals such as anhydrides, isocyanates, silicon-based compounds, aldehydes, epoxides, alkyl chlorides *etc.* have been used for the modification of wood components (Donath *et al.* 2004, Mai and Militz 2004a).

Silicon is the second most abundant element after oxygen. Most of the silicon compounds are classified as non-toxic. A wide variety of organic and inorganic silicon compounds can be applied to wood modification. Inorganic silicon compounds are mainly based on condensation products of silicic acid (colloidal silicic acids, silicates, "water glass") or tetraalkoxysilanes which undergo hydrolysis and condensation steps to form sols and finally gels (sol-gel technology). (Mai and Militz 2004a, Mai and Militz 2004b, Nakayama *et al.* 2001, Furuno and Imamura 1998, Furuno *et al.* 1993, Saka *et al.* 2001, Hager 1995).

In this study, modified wood samples with various colloidal dispersions of silica particles (SiO₂) were tested for laboratory decay resistance, dimensional stability, above ground and ground contact test in Ultuna, Sweden

EXPERIMENTAL

Scots pine (*Pinus sylvestris* L.) specimens were used. Test specimens were treated with colloidal dispersions of silica particles (15 % and 30 %) by 90 % drawing vacuum over the samples for 40 min and 11 bar pressure for 60 min. The specimens were then removed from the treatment solution, weighed to determine uptake retentions for each solution.

Water Absorption Test

Each set of 10 treated wood specimens (15 x 25 x 50 mm) and 20 controls (untreated) were placed into a beaker, and submerged in deionised water. The water was replaced every day for a total of 14 days. The samples were weighed and water absorption values were calculated after each water change.

Fungal resistance tests

Glass jars (500 ml) were filled to three-quarters of their volume with commercial planting soil and sterilized in an autoclave for 60 min at temperature of 120°C and pressure of about 0.1 MPa. Two subsamples and 2 samples (15 x 25 x 50 mm) were placed in each jar. The jars with samples were resterilised under same conditions. After cooling, the samples and soil were inoculated with a 12 ml mycelia suspension of the brown rot fungus *Postia placenta* (FPRL 280). The jars were stored in a climate room at temperature of 25 °C and 65 % relative humidity. The jars were taken after 84 days of exposure, samples were cleaned, dried at temperature of 103 ± 2 °C, weighed and the weight loss was calculated (Eqn. 1).

$$\text{Weight loss (\%)} = [(M_o - M_d) / m_o] \times 100 \quad (1)$$

where

M_o = dry weight prior to test

M_d = dry weight after the test

Field Test

Modified pine samples treated with silicon were exposed to field testing for four years according to standards ENV 12037 and two years for EN 252 in Ultuna, Sweden.

RESULTS AND DISCUSSION

Water absorption values are shown in Table 1. Results shows that all silicon modified wood samples displayed high water absorption values. However, water absorption of silica treated with 30 % was less than silica 15 %. High water absorption can be attributed to hygroscopicity of silicon compounds (Mai and Militz 2004a).

Table 1. Water absorption of silica treated wood

	Immersion time [h]								
	24	48	72	96	168	192	240	264	336
Control	62.20	63.84	64.54	67.99	80.01	83.02	85.84	87	90.55
Silica 15%	61.37	64.21	67	72.55	75.61	76.16	77.64	78.32	80.17
Silica 30%	46.08	48.06	49.36	53.89	57.52	58	58.87	59.36	60.43

Decay resistance against the brown-rot fungus *Poria placenta* is shown in Table 2. According to results, untreated wood specimens were

decayed well by fungi. Wood specimens treated with 15 % silica were well-protected from the attack by *P. placenta*. However, 30 % silica gave high mass loss (Table 2).

Table 2. Weight losses in silica treated specimens after fungal resistance tests (*P. placenta*)

	Treated		Control	
	Average [%]	St. dev	Average [%]	St. dev
Silica 15 %	6.27	4.54	47.55	3.61
Silica 30 %	20.73	2.12	42.06	8.17

The silica impregnated samples in above ground standard lap-joint test and in ground contact were tested according to standards ENV 12037 and EN 252 respectively in Ultuna, Sweden. Lap joint test and ground contact test results are shown in Table 3 and Table 4 respectively.

Table 3: Lap joint results according to ENV 12037- four years

	Upside		Bottom		Joint area	
	Stain	Decay	Stain	Decay	Stain	Decay
Silica	2	0	0	0	0	0
References						
TBTO 1%	3	0	3	0	3	0
CCA 0.8%	1	0	1	0	0	0
Untreated	3	0	3	0	3	0

Table 4. Field test results according to EN 252- two years

	Average
Silica	1
CCA 0.3%	0.4
CCA 1.3%	0
Untreated	1.7

CONCLUSIONS

This study evaluated some laboratory and field test studies of modified wood samples with various colloidal dispersions of silica particles (SiO_2). The silicone impregnated samples showed a durability similar to that of CCA impregnated controls in above ground standard lap-joint test. The durability of the stakes in ground contact was also improved when compared to the untreated controls but exposure time is too short for conclusions.

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CHAPTER 5

OTHER MODIFICATIONS

CHEMICAL MODIFICATION OF WOOD BY O-ALKYLATION

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Keywords: Benzylation, carboxymethylation, methylation, wood, cellulose, lignin, hemicellulose

ABSTRACT

New scientific directions are created in wood chemistry by the simultaneous chemical modification of cellulose, hemicellulose, lignin in the cell wall, which is accompanied by the formation of a composition containing high molecular weight modified components, possessing broad spectrum characteristics. This is a central to making an ecological pure technology.

INTRODUCTION

Studies in the field of the chemical conversion of wood have been performed by us for more than 15 years in the following directions:

- Searching for rational ways for the chemical modification of wood and other raw materials to produce given characteristics
- Methods for the study and analysis of modified wood using Fourier transform IR-spectroscopy, chromato-mass spectrometry, and thermomechanical spectroscopy
- The development of methods to determine the reactivity of the hydroxyl groups of cellulose, hemicellulose, lignin, using kinetic models for the description of the topochemistry of the modification processes.

EXPERIMENTAL

O-alkylation reagents are used for modification, because they interact with of the high-molecular weight cellular components: cellulose, hemicellulose, lignin. We have studied methylation, ethylation, carboxymethylation, benzylation and other reactions. Reagents for modification used industrial reagents, such as: monochloroacetic acid and its sodium-vapor salt, benzylchloride, dimethylsulfate and others.

RESULTS AND DISCUSSION

Carboxymethylation of wood in suspension ambience

We have found (Anon. 1999a) that the reaction of the wood biomass or annual plant materials with ClCH_2COOH or $\text{ClCH}_2\text{COONa}$ is realised in two stages:

- An interaction of the wood with a solution of NaOH
- An interaction of the alkali-wood with ClCH₂COOH or ClCH₂COONa

It is possible to use water, a mixture of iso-propanol and water, or organic solvents as the reaction medium. As a result of reactions of the wood biomass with water-alcohol solution of alkali (2.5 h under 100°C) and ClCH₂COOH or ClCH₂COONa (55° C, 2 h) the product is formed with a high solubility in water and a carboxymethyl groups per cent content of 27.5%.

The carboxymethyl groups percentage content and solubility in water of products depend upon the nature of the solvent, which used for undertaking the reactions (Markin *et al.* 1998). Variation of the nature of the solvent allows for the possibility to realise the directional syntheses of the products with a given characteristic.

We have determined that the length and the temperature of the preliminary alkaline processing (Markin *et al.* 1998a, Markin *et al.* 1999b) renders the defining influence upon characteristics of the products to reactions: the contents of -CH₂COOH groups (CMG), solubility and relative viscosity of the alkaline solution.

Carboxymethylation of wood by solid-phase method

Carboxymetylation is realised by the solid-phase method in a different mill (Anon. 1999b, Anon. 1999c). As a result of the solid-phase carboxymetylation of wood and plant raw material in a ball mill in one stage is received the products, containing in their composition 8.9–20.5 % CMG, with solubility in water of 80–98 %. The products having a higher viscosity in alkaline solution can be produced using a reaction mixture of water 0.3–1 h, or by reducing the particle size by milling (Markin *et al.* 1997).

The products of carboxymethylathion, obtained directly from plant raw material, contains in its composition carboxymethylated cellulose, hemicellulose, lignin and can find use as a chemical reagent, alongside with carboxymethylated cellulose (Markin *et al.* 1997, Bazarnova *et al.* 1998).

Benzilation of wood

The reaction of wood benzilation is realised in two stages:

- An interaction of wood with solution of alkali
- An interaction of alkali-wood with benzylchloride

The product of the reactions is a light-yellow powder. The content of benzyl groups depends on length and the temperature of reactions (Likasov *et al.* 1997). The main reaction ends after 2–2.5 h. The products are soluble in acetone and dioxan (partially), and in chloroform practically completely (Katrakov 1999).

The product, containing 33.4 % of the benzyl groups exhibits an intensive loss of mass at 180°C, 40°C lower than for unmodified wood. This allows for its use as a thermoplastic adhesive (with concentration 10–30 %) for the preparation of composites by using hot pressing at 120–180°C (Katrakov 1999). It is possible to make composites using wood

material and with mineral filler (marble and brick dust, reduced glass). These are of a comparable quality to wood composites bonded with phenolformaldehyde resin (Likasov *et al.* 1997).

Methylation of wood

Consequent or simultaneous processing of wood with alkali and $(\text{CH}_3)_2\text{SO}_4$ is accompanied by the formation of methylated celluloses and hemicellulose with a small quantity remaining of lignin, which is determined by method of UV spectroscopy.

The products of the methylation of wood are formed when undertaking the reactions, as a suspension and in a ball mill without accompaniment of the solvent. Products are formed with the contents of CH_3O groups of 10–28 %, and with a solubility in water of 90–98 %.

The methylated polysaccharides can find use, alongside methylcellulose, in the production of the building materials and in the other areas.

The reaction topchemistry in the cell wall

The cellulose reacts to a lesser extent, than the lignin and hemicellulose for the carboxymethylation reaction of wood (Markin *et al.* 2000). The reactivity of components during the benzylation of wood decreases in the following order: cellulose, (holocellulose), (wood), 4-*O*-methylglucuronicxytan and dioxan-lignin (Katrakov *et al.* 1997).

The degree of hemicellulose transformation was investigated for the example of benzylation and carboxymetylation and confirmed the presence of unsubstituted monosaccharides, formed as a result of the hydrolysis of modification wood. The degree of hemicellulose transformation was comparable. The products of the methylation of wood contains in its composition both methylated and unmethylated polysaccharides (Korinova 2004).

The degree of substitution of cell wall bound lignin lower, than that of isolated lignin for carboxymethylation. The reactivity OH-groups of lignin during carboxymethylation, changes as follows: $\text{OH}_{\text{phen.}} > \text{OH}_{\text{second.}} > \text{OH}_{\text{first}}$ (Markin *et al.* 2000, Markin *et al.* 2001).

FTIR was used for a systematic study of benzylated and carboxymethylated celluloses, lignin and wood (Karpova 2002, Bazarnova 2002). The spectral studies show that reaction derived wood contains in its composition substituted cellulose, lignin, hemicellulose. However, the substitution is not realised evenly. It is noted that in the process of benzylation and carboxymethylation of cellulose in wood, the reactivity of OH-groups decreases in the order $\text{C}_6 > \text{C}_2 > \text{C}_3$.

CONCLUSIONS

The study of chemical modifying (carboxymethylation, benzylation, methylation) of the structural components directly in plant cell into high-molecular bio-compositions with set properties (thermoplasticity, water or solvent solubility *etc.*) is a fact from both ecological and economic points of view. As a result of chemical reaction search it was stated that series of modifying reagents, which in use for obtain cellulose ethers, and suitable optimisation of the reaction conditions could be successfully used for obtaining of the high-molecular

compositions as a products of direct modifying of wood. These products have a set of practical uses.

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MODIFICATION OF WHEAT STRAW WITH THE WHITE-ROT FUNGUS *PLEUROTUS OSTREATUS* FOR APPLICATION IN NATURAL FIBER REINFORCED THERMOPLASTIC COMPOSITES

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ABSTRACT

The predominant filler used in the commercial production of natural fiber reinforced thermoplastic composites is wood flour. Fibres such as wheat straw (*Triticum aestivum* L.) represent a promising filler alternative due to their abundant availability, cost-efficiency, and inherent material properties. In this study, the feasibility of using wheat straw as a filler in high-density polyethylene (HDPE)-based composites was explored. Straw was treated with the white-rot fungus *Pleurotus ostreatus* with the aim of improving adhesion between straw and plastic, and thereby the mechanical properties of the composite. Results indicate that the use of sterilised straw is necessary to inhibit the growth of indigenous organisms that preclude, likely through competition, removal of lignin, and hence, improved bonding between straw and plastic. Reduced thermal stability of treated straw did not negatively affect the production of injection-molded straw-plastic composites. Dynamic mechanical analysis demonstrated that similar storage and loss moduli were obtained for composites based on untreated straw and pine flour.

INTRODUCTION

Extruded wood-plastic composites (WPC) have recently experienced significant market growth in North America, primarily for application as deckboard (Wolcott and Englund 1999, Clemons 2002). Wheat straw (*Triticum aestivum* L.) offers potential for use as filler instead of wood resulting in the manufacture of straw-plastic composites (SPC). Wheat straw is an annually renewable agricultural by-product. In the United States alone, 60 million MTs of wheat straw are currently produced every year, 99 % of which are either returned to the field by burning, tilling into the soil, or used as an on-farm fuel source (Cheng *et al.* 2004). The use of wheat straw in the production of natural fiber-reinforced thermoplastic composites potentially generates a new revenue stream for wheat producers, provides an incentive to reduce air pollution caused by field-burning, and accomplishes soil conservation goals in arid climates. However, straw utilisation for composites is limited by poor resin and polymer penetration, and excessive resin

consumption owing to the straw cuticle, fines and the lignin-hemicellulose-matrix (Houghton *et al.* 2004). Some white-rot fungi, including *Pleurotus ostreatus*, degrade the cuticle and selectively degrade lignin and hemicelluloses, leaving behind relatively more cellulose (Houghton *et al.* 2004, Valmaseda *et al.* 1991, Moyson and Verachtert 1991, Gamble *et al.* 1996). Thus, treatment of wheat straw with *P. ostreatus* could potentially be used to improve resin penetration into the straw without the use of physical or chemical pretreatments. In addition, straw treatment with *P. ostreatus* was expected to (1) improve adhesion between the straw and plastic, and thereby the mechanical properties of a composite material; and (2) possibly reduce the amount of polyethylene required in the production of high-density polyethylene-based composite materials, and hence, the cost of the composite product.

The overall goal of this study was to explore the feasibility of using fungal-modified wheat straw as filler in high-density polyethylene (HDPE)-based composites. The specific objectives of this study were to:

- Characterise physical, chemical, thermal and morphological properties of wheat straw following treatment with *P. ostreatus*;
- Evaluate the influence of straw sterilisation on the effectiveness of straw degradation by *P. ostreatus*;
- Prepare injection-molded straw-plastic composites (SPC) from fungal-modified and non-modified wheat straw; and
- Perform dynamic mechanical analysis (DMA) on SPC and determine activation energies for the α -transition of HDPE in SPC.

EXPERIMENTAL

Wheat Straw

A hard red spring variety of wheat straw (*Triticum aestivum* var. Westbred 936), obtained from Grant 4-D Farms (Rupert, ID) during the year 2000 cropping season, was used in all experiments. Straw stems were mechanically separated and stored indoors at $21 \pm 2^\circ\text{C}$ and 13 % moisture content until used (Houghton *et al.* 2004). Overall straw stem length was less than ~ 10 cm with typical values ranging from 5 and 10 cm. Some of the straw used in the experiments was chopped through a screen with a 1.78 cm-hole-diameter using a Nelmor-chopper.

Preparation of Fungal Inoculum

Pleurotus ostreatus ATCC 32783 was chosen based on its lignin-degrading activity (Haider and Trojanowski 1975). Fungal stock cultures were maintained at Utah State University on agar slants containing 41 g yeast-malt (YM) agar (Becton, Dickinson and Company, Sparks, MD) per L of water. Fresh slants were prepared and inoculated every two weeks. Slants were incubated at room temperature with caps loosely attached. Mycelia from two- to three-week old slants were used to inoculate 100 ml of liquid starter cultures in 500 ml Erlenmeyer flasks equipped with cotton plugs. Liquid starter cultures, containing 21 g YM broth (Becton,

Dickinson and Company, Sparks, MD) per L of water, were autoclaved, and stock mineral solution was added (10 ml per L of YM broth). Stock mineral solution (100X) consisted of 3.0 g of $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$, 0.5 g of $\text{MnSO}_4 \cdot \text{H}_2\text{O}$, 1.0 g of NaCl, 0.1 g of $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$, 0.1 g of CoSO_4 , 0.1 g of $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$, 0.1 g of $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$, 0.01 g of $\text{NaMoO}_4 \cdot 2\text{H}_2\text{O}$, 0.01 g of $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$, 0.01 g of $\text{AlK}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$, 0.01 g of H_3BO_3 per one L of water (all chemicals were standard laboratory grade). To this solution, 1.5 g/L nitrilotriacetic acid (NTA) was added and the pH adjusted to 6.5 with KOH. The stock solution was filter-sterilised and stored at 4°C.

Starter cultures were incubated for two to three days at room temperature in a metabolic shaker (New Brunswick Scientific Series 25, Edison, NJ) at ~200 rpm. After sufficient growth, the starter cultures were aseptically transferred to 2.8 L Fernbach flasks containing 1.5 L of liquid culture medium (same as for starter cultures) and incubated as previously described for three to four days. Fungal pellets were separated from medium by centrifugation (Sorvall RC-5B) at ~10,000xg for 10-15 minutes and transferred to sterile 500 ml bottles with sufficient spent medium to submerge the pellets. These bottles were shipped under refrigeration to Washington State University and stored at 4°C until use (no longer than two weeks from date of arrival).

Fungal Inoculation, Incubation and Processing of Wheat Straw

Wheat straw was treated with different amounts of fungal inoculum and sterile, distilled water (Table 1). For each treatment, with the exception of #12, #13 and #14, 100 g of wheat straw were placed in each of three 53.3 x 21.0 x 12.1 cm mushroom spawn bags (Myco Supply, Pittsburgh, PA), equipped with a 0.3 µm filter patch which allowed gas exchange while simultaneously precluding the passage of contaminants during incubation. To prepare the fungal inoculum for application to the wheat straw, 500 ml of inoculum in spent medium were transferred into a sterile blender (Waring, Torrington, CT), and 50 ml sterile, distilled water were added to aid homogenisation. The solution was homogenised in the blender for 30 seconds at low speed setting. Sixty ml of sterile, distilled water were added to each bag to obtain a straw moisture content (MC) of ~70 % (based on dry weight). The desired amount of inoculum, containing 8.9 +/- 0.8 mg fungal dry weight per ml culture, was then added to each bag using a sterile pipette. The bags were sealed using an electronic impulse sealer and well shaken. Fungal dry weight was determined by adding 30 ml of remaining homogenized inoculum to each of three dried and weighed 50 ml centrifuge tubes. The tubes were spun for twenty minutes at 6°C and 35,300xg in a centrifuge (Beckman J2-HS, Fullerton, CA), weighed to the nearest 0.001 g, and the supernatant was decanted. Following oven-drying at 80°C for 12 hours, the tubes were re-weighed and fungal dry weights calculated.

Some of the straw was chopped and/or autoclaved prior to inoculation (Table 1). Prior to autoclaving, straw (100 g) was placed in aluminum pans and covered with aluminum foil. The pans were then autoclaved for 40 minutes at 121°C and transferred to a laminar flow cabinet to dry overnight. The straw was transferred from the pans into spawn bags and autoclaved for 20 minutes at 121°C. The bags were again placed in the laminar flow cabinet and immediately inoculated following the procedure described above.

A control, consisting of 60 ml sterile, distilled water and 120 ml growth medium, was included in the experiments (treatment #11, Table 1). A bleach (6 % sodium hypochlorite) treatment (#12) was also included to determine its effectiveness in straw delignification. For the bleach treatment, 100 g of straw was added to each of four aluminum pans. One gallon of distilled water and 150 ml bleach were added to each pan. The straw in the pans was submerged in this solution for five hours, rinsed with distilled water twice and oven-dried.

Table 1: Experimental matrix used to identify conditions that promote the growth of *P. ostreatus*^a.

Treatment #	Sterile, distilled water (ml per bag)	Inoculum (ml per bag)	Straw autoclaved	Straw chopped (0.7" screen)
1	60	30	no	no
2	60	30	no	yes
3	60	30	yes	no
4	60	60	no	no
5	60	120	no	no
6	60	120	yes	yes
7	0	120	no	no
8 ^b	20	60	no	no
9 ^b	50	30	no	no
10 ^b	65	15	no	no
11	60	n.a. ^c	no	no
12	n.a. ^d	n.a. ^d	no	no
13	0	0	no	no
14	0	0	yes	no

^a Each treatment was performed in triplicate. All treatments were incubated in mushroom spawn bags, except for #12, #13 and #14.

^b Sterile distilled water and inoculum were mixed prior to application on straw. In all other treatments, water and inoculum were added consecutively to the straw.

^c 120 ml growth media were added instead of inoculum.

^d Treatment #12 consisted of 6% sodium hypochlorite (bleach). For a description of application, please see text.

All bags were incubated at 24°C and 65 % relative humidity for three months. Following weight loss and moisture content (MC) measurements (described below), the straw was ground in a laboratory mill (Thomas-Wiley®, Model 4, Thomas Scientific, Swedesboro, NJ) equipped with a 1 mm screen and stored at 4°C until use in either analyses of straw properties or production of straw-plastic composites.

Analysis of Selected Properties of Wheat Straw

Weight Loss and Moisture Content (MC)

At the end of incubation, the straw was weighed, oven-dried until constant weight was reached and re-weighed to determine dry weight and moisture content (MC). Moisture content was calculated using Equation (1):

$$MC (\%) = ((W_w - W_D) / W_D) \times 100 \quad (1)$$

Where: W_w = wet weight of straw (g) and W_D = dry weight of straw (g).

The effectiveness of fungal degradation was estimated as the weight loss (on a dry-weight basis) over the three-month incubation period for treatments #1 to #11.

Thermogravimetric Analysis (TGA)

Ground straw samples were dried in a vacuum oven at room temperature overnight to obtain a straw MC between 5 and 7 %. Thermogravimetric analysis was then performed using a simultaneous thermal analyser (Rheometric Scientific STA 625, Piscataway, NJ). Straw samples of approximately 4 mg weight were heated in an aluminum pan (Rheometric Scientific L7168 2mm, Piscataway, NJ) to 580°C at a heating rate of 60°C per minute. The maximum temperature (580°C) was held for 20 minutes, followed by cooling to 30°C at a rate of 60°C per minute. Each sample was run in duplicate. After each TGA-run, the data obtained were converted from the Rheometric software (RSI Orchestrator, Version V6.5.5) into an Excel-file, and weight losses were calculated based on the original sample weights with correction for the buoyancy effect of the air.

Chemical Analyses

Carbohydrate and lignin analyses were performed on approximately 350 mg of oven-dried material of treatments #4, #5, #6, #11, #12, #13 and #14 from the spawn-bags (Table 1). Individual monosaccharides (araban, xylan, mannan, galactan and glucan) were separated on a glass column packed with 3 % cyanopropyl silicone (SP-2340, (Supelco, Bellefonte, PA) in a gas chromatograph (Hewlett-Packard 5890, Series II, Wilmington, DE) at 205°C following sulfuric acid hydrolysis according to TAPPI Method T 249 cm-85. One sample of each treatment was analyzed in duplicate chromatographic runs. Acid-insoluble Klason lignin for one sample of each treatment was determined according to Effland (1977).

Production of Straw-Plastic Composites (SPC)

Treatments #5, #6, #13, #14 and a control consisting of 60-mesh Southern yellow pine flour were compounded and processed into thermoplastic composites. Sixty percent (by weight) of individual fiber treatments and 40 % (by weight) of high-density polyethylene powder (Equistar Chemical LBO10000, Houston, TX) were thoroughly mixed by shaking in a plastic bag and then compounded into pellets at 180°C and 20 rpm in a Haake PolyLab System (Rheocord 300p and Rheomix 600p, Thermo Haake, Karlsruhe, Germany), equipped with roller rotors. Processing time was approximately 5 min. for each batch. Pellets were added to a screw-driven capillary extrusion rheometer (Acer 2000, Rheometric Scientific, Piscataway, NJ), equipped with a non-commercial die, soaked for 30 min. at 180°C, and injection-molded into samples (nominal dimensions: 1.4 mm thickness, 6 mm width, 45 mm length) for dynamic mechanical analysis (DMA). Density of DMA-specimens prepared from treatments #5, #13 and pine flour was 1.34 +/- 0.02 g/cm³ whereas density of samples based on treatment #6 and #14 were 1.39 +/- 0.01 g/cm³ and 0.93 +/- 0.04 g/cm³, respectively.

Dynamic Mechanical Analysis (DMA) of Straw-Plastic Composites

Dynamic mechanical analysis was conducted in dual cantilever mode in a Rheometrics RSA II solids analyser (Piscataway, NJ). Initially, dynamic strain sweep tests from 10⁻⁴ to 10⁻³ were run at -50, 25 and 100°C to ensure linearity throughout the test. Dynamic temperature scans from -50°C to +100°C were conducted at sequential frequencies of 0.1 Hz, 1 Hz and 10 Hz and a strain of 10⁻⁴. In all experiments, the heating rate was 2°C per minute, and the soak time was one minute.

The activation energy for the α -transition of SPC was calculated using the Arrhenius equation (Turi 1997):

$$k = A_e \exp [- E_a / RT] \quad (2)$$

Where: k = rate constant or test frequency; A_e = frequency factor; R = ideal gas constant; 8.314 J/(mol K); T = temperature (K); E_a = activation energy. The peak temperatures of E'' at different frequencies were calculated using software (RSI Orchestrator, version V6.5.5, Rheometric Scientific, Piscataway, NJ).

Statistical analysis was conducted to determine if the differences in activation energy required for α -transition were significant at a 95 % confidence level for SPC based on treated and untreated straw. A Tukey-Kramer Multiple-Comparison ANOVA Test was performed with Number Cruncher Statistical Software (Kaysville, Utah).

RESULTS AND DISCUSSION

Visual Observations of Fungal Colonization on Wheat Straw

It was determined by visual observation that *P. ostreatus* successfully colonised straw only when sterilised straw was used. After approximately two weeks of incubation, abundant fluffy, white *P. ostreatus* mycelium was observed in the spawn bags containing sterilised straw. It was observed in additional experiments that colonisation of sterilised straw was only successful when the straw had been chopped prior to sterilisation and inoculation.

In all treatments in which unsterilised straw was used, the straw was colonised by a plethora of microfungi. No attempt was made to isolate and identify the fungi present since this was beyond the scope of the project.

Analysis of Selected Properties of Wheat Straw

Weight Loss and Moisture Content (MC)

Although weight loss was observed in treatments #1 through #11 (Figure 1), weight loss values are not necessarily indicative of the effectiveness of fungal degradation. This is primarily due to the fact that fungal mycelia on sterilised straw in treatment #6 could not be separated from the substrate following incubation, thus potentially producing an underestimate of the effectiveness of degradation.

The relatively high weight losses in treatments #5, #6 and #11 (Figure 1) correspond to treatments that had comparatively high straw MC (more than 150%) after inoculation (data not shown), suggesting MC (either as a threshold value or a continuum) influenced degradation. Weight loss of straw treated with growth medium (#11) was overall as high or higher than weight loss of unsterilised straw inoculated with *P. ostreatus* (treatment #5, Figure 1); hence, inoculation of unsterilised straw with *P. ostreatus* was likely not an effective component in the observed weight loss.

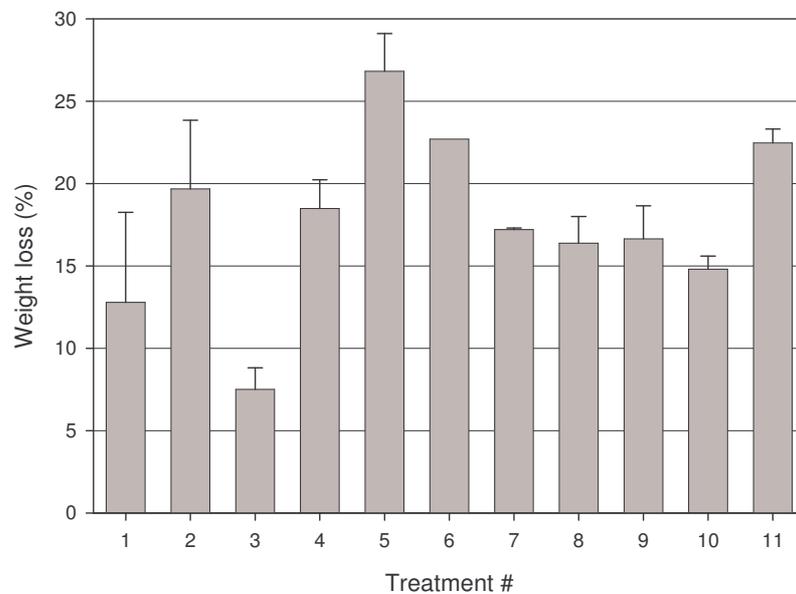


Figure 1: Weight losses of wheat straw obtained with treatments #1 to #11 (see Table 1 for description of treatments; weight loss of treatment #6 was determined with one replicate only, hence, no error bar shown). Error bars represent the standard deviation for triplicates of each treatment.

Thermogravimetric Analysis (TGA)

Thermogravimetric analysis (TGA) was used in this study to determine if a change in the chemical composition due to fungal degradation of the straw had an effect on its thermal stability. Thermogravimetric analysis is a technique for measuring the weight loss of a substance as a function of temperature. It has previously been employed to identify changes in the components of mushroom and straw compost (Sharma 1990 and 1996, Blanco and Almendros 1994, 1997) and to evaluate fungal degradation of wood (Beall *et al.* 1976). Thermogravimetric analysis showed that the highest weight losses of straw occurred in the temperature range between 200°C and 350°C, followed by a less active pyrolysis stage which ranged from 350°C to 600°C (data not shown). Initial substrate weight losses in the low temperature range of up to 100°C can be attributed to dehydration. These results, overall, are comparable to findings by Sharma (1990) who investigated straw degraded by *P. ostreatus* after 20 and 40 days of incubation.

In the temperature ranges between 260°C and 330°C and between 380°C and 580°C, the relative weight losses of sterilised straw inoculated with *P. ostreatus* were higher than those of unsterilised-inoculated straw (data not shown), suggesting that a higher level of fungal degradation was achieved with sterilised straw. However, the straw thermal behavior may have been influenced by the large amount of fungal biomass present in the sterilised and treated straw.

The observed reduced thermal stability of sterilised-treated straw did not noticeably affect the production of straw-plastic composites based on this filler material.

Chemical Analysis

Results from carbohydrate analyses (Table 2) were used to estimate the amounts of hemicelluloses and cellulose in straw. Glucan is the dominant carbohydrate which mostly makes up the cellulose. However, a portion of the glucan is combined with mannan in the hemicellulose fraction. The ratio between glucan and mannan is 1:2. The hemicellulose content was therefore estimated as the sum of all non-glucose sugars plus $\frac{1}{2}$ of the mannan fraction for each sample (Table 3). Cellulose content was estimated as the sum of the glucan value minus $\frac{1}{2}$ of the mannan fraction. The dominant non-glucose carbohydrate in hardwoods as well as in wheat straw is xylan. The total sum of the hemicellulose, cellulose and lignin fractions is less than 100% (Table 3) due to extractives, crude protein, ash and silica present in the straw.

Unsterilised, untreated wheat straw contained 21.3 % lignin and therefore less lignin than most wood species (Fengel and Wegener 1989). The amount of lignin in straw determined in this study is comparable to results by Muller (1960) who found 18.2% lignin in the internodes of summer wheat and 20.2 % lignin in winter wheat. The greatest reduction in lignin was achieved in the sterilised, inoculated straw (Treatment #6, Table 3). Sterilised, inoculated straw contained 17.4 % lignin and thus, 24 % less lignin than sterilised, non-inoculated straw (22.8 %). Inoculation of unsterilised straw with *P. ostreatus* did not reduce the amount of lignin in the straw, and neither did the addition of growth medium or bleach (Table 3). In addition, fungal treatment of sterilised straw did not reduce the amount of cellulose and hemicelluloses in the straw and was therefore shown to be selective for lignin. Inoculation of unsterilised straw with *P. ostreatus* reduced cellulose by up to 12 % and hemicelluloses by up to 13% but did not result in reduction of lignin.

Overall, the lowest amount of hemicellulose was determined in sterilised, non-inoculated straw. This can be explained with the autoclaving procedure which is comparable to steam-explosion treatment, albeit performed at lower pressure. It has long been known that steam-explosion solubilises large amounts of sugars in wood (Saddler *et al.* 1982) and wheat straw (Vallander and Eriksson 1985). In fact, some monosaccharides were probably lost in all straw samples during the autoclaving step which is part of the sulfuric acid hydrolysis.

Table 2: Carbohydrate composition of straw at the end of a three-month incubation under different treatment scenarios

Treatment	Weight of specified compound /Weight of oven-dried straw (%) ^a				
	Arabinan	Xylan	Mannan	Galactan	Glucan
Sterilised, inoculated (#6)	2.4	17.6	2.1	0.7	33.7
Sterilised, not inoculated	2.7	14.4	1.3	0.8	27.4
Not sterilised, inoculated (#5) ^b	2.3	16.2	1.3	0.9	28.3
Not sterilised, inoculated (#4) ^c	2.5	18.4	1.3	0.8	31.1
Not sterilised, not treated	3.0	18.8	1.2	0.8	32.2
Growth media (#11)	2.6	18.0	1.2	1.1	31.6
Bleach (#12)	3.3	17.5	1.1	0.9	31.7

^a Each value represents the average of two chromatographic runs of one sample.

^b 120 ml inoculum.

^c 60 ml inoculum.

Table 3: Cellulose, hemicellulose and lignin composition of straw at the end of a three-month incubation under different treatment scenarios

Treatment	Weight of specified compound/Weight of oven-dried straw (%)		
	Hemicellulose ^a	Cellulose ^a	Lignin ^b
Sterilised, inoculated (#6)	23.8	32.7	17.4
Sterilised, not inoculated	19.9	26.8	22.8
Not sterilised, inoculated (#5) ^c	21.2	27.7	28.4
Not sterilised, inoculated (#4) ^d	23.6	30.5	25.9
Not sterilised, not inoculated	24.3	31.6	21.3
Growth media (#11)	23.5	31.0	25.4
Bleach (#12)	23.4	31.1	22.6

^a Each value represents the average of two chromatographic runs of one sample.

^b Each value represents the result from a single sample.

^c 120 ml inoculum.

^d 60 ml inoculum.

Dynamic Mechanical Analysis of Straw-Plastic Composites

Dynamic mechanical analysis (DMA) can provide valuable molecular and morphological information about a material in the solid state by subjecting it to dynamic loads over a broad range of temperature and frequency (Saini and Shenoy 1985). During measurement, a sinusoidal strain is applied to the sample, while measuring the sinusoidal stress response. A portion of the response output is in phase with the strain input and represents the energy stored in the material or the elastic component (E' , storage modulus). The remaining response is out of phase with the strain and represents the energy dissipated by the material or the viscous component (E'' , loss modulus).

A phase transition was noted by a peak in the loss modulus between 30 and 65°C, depending on the frequency and filler treatment (data not shown). This peak represents the α -transition of polyethylene (Ward and Hadley 1993). Relaxation transitions in polymers are labeled as α , β , γ etc. in alphabetical order with decreasing temperature. The γ -transition corresponds to the glass transition temperature of PE (Kosfeld *et al.* 1981). In HDPE, the β -transition is usually absent (Sirotkin and Brooks 2001). The α -transition in PE corresponds to the molecular segmental motion in the crystalline phase, *i.e.*, chain rotation (Saini and Shenoy 1985).

Activation energies for the α -transition in individual SPC and the pine-based composites were calculated using Arrhenius plots. The activation energies obtained for the α -transition in our SPC are comparable to literature values for various polyethylenes and polyethylene-based composites (Matsuo *et al.* 2003, Vaisman *et al.* 2003). Minimal differences were observed between the DMA-spectra for unsterilised, treated and unsterilised, untreated straw (Figure 2). This indicates that treatment of unsterilised straw did not result in an improvement in the straw-HDPE interphase. Activation energies of the SPC and the composite based on pine flour were similar. It can be concluded that similar interfacial adhesion was obtained for untreated straw- and pine-based thermoplastic composites.

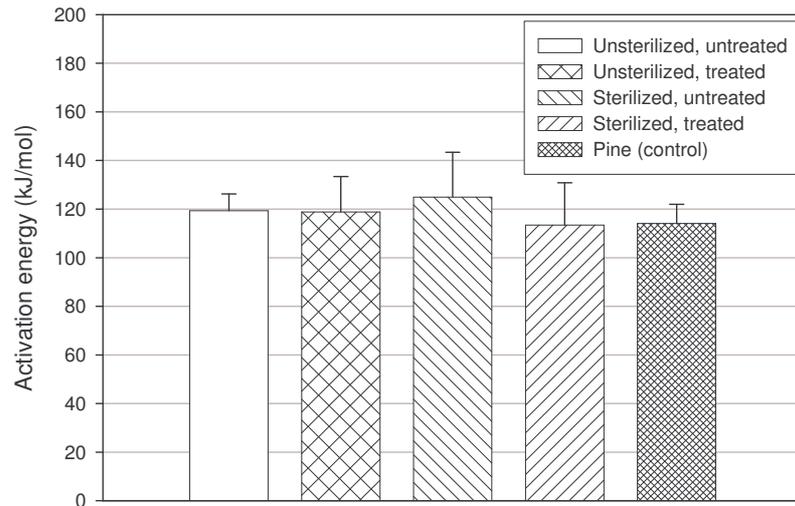


Figure 2: Activation energies for α -transition of HDPE in injection-molded straw-plastic composites (SPC) based on straw from mushroom spawn bags and one wood-plastic composite based on unmodified pine flour. Data were collected in frequency-temperature scans performed from -50°C to $+100^{\circ}\text{C}$ at simultaneous frequencies of 0.1 Hz, 1 Hz and 10 Hz. Each bar represents the average of three values for activation energy obtained in individual frequency-temperature scans. Error bars represent the standard deviation for each treatment. Straw-plastic composites made with treated and untreated straw were not significantly different at a 95% confidence level based on a Tukey-Kramer Multiple-Comparison ANOVA Test.

CONCLUSIONS

Inoculation of unsterilised wheat straw with *P. ostreatus* did not result in dominance of *P. ostreatus* on the straw under the conditions applied in the present study. When straw was sterilised prior to fungal inoculation, *P. ostreatus* dominated over existing microorganisms. Reduced thermal stability of treated straw did not negatively affect the production of straw-plastic composites. Fungal treatment of sterilised straw did not reduce the amount of cellulose and hemicelluloses in the straw and was therefore selective for lignin. In contrast, fungal treatment of unsterilised straw with *P. ostreatus* was not selective for lignin. Dynamic mechanical analysis indicated that similar interfacial adhesion was obtained for untreated straw- and pine-based thermoplastic composites. The results obtained in this study demonstrate that wheat straw represents a promising alternative to wood fillers in the production of wood plastic composites (WPC).

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SCREENING OF PROPERTIES OF MODIFIED CHITOSAN-TREATED WOOD

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Keywords: Anaerobe, anti-fungal, chitosan, heat-treated, hydrophobation, mechanical properties.

ABSTRACT

Chitosan is a biopolymer derived from chitin in crustacean shells and has in the last decade been studied as an environmental benign wood protecting agent. It is proposed to act as a fungistat against a wide range of fungi and even as a fungicide at higher concentrations. The topic of this paper is to investigate the wood modifying properties of chitosan with different molecular weights. Scots pine (*Pinus sylvestris* L.) and beech (*Fagus sylvatica*) samples were impregnated with two chitosan solutions differing in their average molecular weights. The chitosan solutions were depolymerised by nitrous acid to one of high and one of low molecular weight solution with a concentration of 5 % (w/v). The untreated samples, chitosan treated samples and modified chitosan samples were investigated for their water sorption properties, hardness, modulus of elasticity, static bending and impact bending. In addition the samples underwent a fungal trial with *Trametes versicolor* and *Coniophora puteana* in a modified EN 113 test of 8 weeks duration. This paper shows the changes in sorption properties, anti-fungal properties and mechanical properties of modified chitosan treated wood. Heat modified chitosan treated wood shows similar properties like chitosan treated wood, but the wood gets a brownish colour, the hydrophobation is enhanced and the anti fungal properties as slightly reduced. MOE is enhanced and the MOR shows no change.

INTRODUCTION

Wood in use outdoors or in humid condition is in danger of being attacked by wood deterioration micro-organisms, like fungi. To prolong the life time of wood in use, it is required to protect the wood against these micro-organisms. One way to achieve this is to pressure impregnate wood with chemicals, or modify the wood itself, to enhance the natural durability of the wood. It has been reported in the last 25 years that the production, treatment and waste management of wood protective chemicals and chemical protected wood or modifications has given a negative impact to the environment. It is therefore needed an intensified research area in develop new, more environmentally friendly wood preservatives.

This paper describes a new method to protect wood in an environmental friendly approach. The protection of wood from fungi by the means of chitosan has been intensively researched in the last four years. (Laflamme *et al.* 1999, Mehrtens 1999, Frederiksen 2001, Chittenden *et al.* 2003, Larnøy *et al.* 2005, Alfredsen *et al.* 2004, Eikenes *et al.* 2005) Chitosan, a natural polymer, is a non-toxic, edible, and biodegradable deacetylated product of chitin. It is a naturally occurring polysaccharide which has been found in a wide range of natural sources

(crustaceans, fungi, insects, annelids, molluscs, coelenterate *etc.*) (Muzzarelli 1990). Chitosan is normally manufactured from crustaceans (shrimp, crab, krill and crayfish), primarily because a large amount of the crustacean exoskeleton is available as a by-product of the food-processing industries (Brine *et al.* 1991). Chitosan consists of β -1,4-linked D-glucosamine residues with a variable number of randomly located N-acetyl-glucosamine groups. Chitin, a β -1-4 linked polymer of 2-acetamido-2-deoxy-D-glucose, is the most abundant natural nitrogen-containing polysaccharide, and its annual bio-production is estimated to be almost as much as that of cellulose (Kumar 2000), at a level of up to 1–10 billion tons per year (Ratajska *et al.* 1997).

During some trials of fixation of chitosan, a new side of chitosan treated wood was detected. By heating chitosan impregnated wood directly after impregnation under anaerobic conditions, the sample turned dark brown and became hydrophobic in an EN 84 test. The properties of this new product was studied closer and presented in this paper. There have been no earlier studies on this theme.

EXPERIMENTAL

Chitosan production

The chitosan solutions were prepared from industrial chitosan flakes by depolymerisation with nitrous acid (Allan and Peyron 1995). Chitosan was dissolved in water with addition of acetic or hydrochloric acid to pH 5.5. The chitosan solutions were mixed well in a concrete blender, and when all chitosan was dissolved a 4 % (weight/volume) aqueous solution of potassium nitrite or hydrogen peroxide was added by spraying a fine mist onto the chitosan solution while continuously mixing at 30°C. After 5 hours the solution was transferred to a barrel and stored at ambient temperature.

Wood samples

Sound samples of Pine (*Pinus sylvestries*) and Beech (*Fagus sylvatica*) without defects were used. The annual rings had an angle close to 90°. For testing of the water uptake, samples of 10_r x 25_t x 50_l mm³ was used. In the modified EN 113 trials, samples with the dimensions of 5_r x 10_t x 30_l mm³ were used. Finally, samples with the dimensions 20_r x 20_t x 360_l mm³ were used for MOE / MOR

Impregnation of the wood samples

The wood samples were weighed and impregnated using the following processes: The samples were placed in the impregnation chamber and evacuated for 1 hour at 100 mBar followed by 1 hour at a pressure of 12 Bars, The pressure was then released and the samples rinsed under water and wiped off with a cloth before the weight was recorded.

Heat treatment

To achieve the wanted modification by heat, samples were wrapped in a cooking bag and sealed to avoid evaporation of air and thereby keeping it anaerobic. Different temperatures of 60, 80 and 100°C and process times of 36, 48 and 60 hours were used

Exposure to water

The samples were submerged in water and weighed down. The samples were then weighted regularly during a time interval of 7 days. The samples was coded as *e.g.* P_80_60_L witch here means that these samples was of pine and impregnated with low molecular weight chitosan, heat treated at 80°C for 60 hours

Test of anti-fungal properties

Samples of pine and beech were exposed to *Coniophora puteana*, *Poria placenta* and *Trametes versicolor* for 8 weeks in a modified EN 113 test. The samples were placed in Petri discs. Each disc contained 6 samples and 3 discs per variable which gives n=18. The initial dry weight was recorded as were the dry weights after exposure. By evaluating these two sets of data, the mass loss was recorded. The moisture content was calculated on the basis of the dry weight after fungal exposure. To determine the uptake of chitosan in the samples, the weight was recorded before and after impregnation and calculated with the size of the samples to get the answer in Kg/m³. To evaluate if the protonic acid or the depolymerising agent has an influence on the mass loss, two different chitosan solutions were used. One with hydrochloric acid and hydrogen peroxide and the other with acetic acid and potassium nitrite.

Test of mechanical properties

The modulus of elasticity and the modulus of rupture were tested on a Zwick 010 test bench. The samples were conditioned at 20°C and 65 % RH until stable weight was achieved. Samples of untreated pine and beech wood were tested against chitosan treated samples, pigmented chitosan samples and samples heat treated at 80°C of 60 hours. The pigmented chitosan samples were tested as a part of future investigations to see if the pigmentation gives any change in the wood properties.

RESULTS AND DISCUSSION

Water uptake

As seen in Figure 1, the result showed a rapid and high rise in the moisture content of the untreated wood samples within the first hour followed by a slower rise until 80 % moisture content after 24 hours. The modified chitosan treated wood samples showed an improvement in the area of 50 % to 20 % lower moisture content. The samples treated with high molecular weight chitosan showed a slightly better hydrophobation of approximately 10 % compared to the low molecular weight chitosan. The samples treated for 60 hours showed some better hydrophobation with an increase of approximately 5 % compared to the samples treated for 48 and 36 hours whom only showed a small difference to each other.

Although the heat modified chitosan treated samples showed a good reduction in water uptake, they will eventually after approximately one week in water achieve the same moisture content as untreated samples. This showed that this treatment is not water repellent, but slows down the water uptake. This might although, give a good enough water repellent effect to keep the wood in use dry. And therefore gives an additional protection against wood destroying micro-organisms.

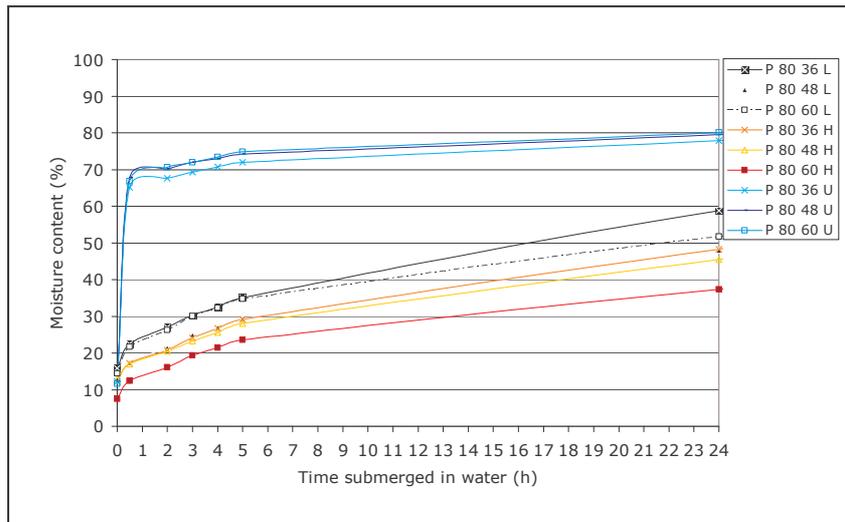


Figure 1: Water uptake of untreated pine samples, pine samples treated with low molecular chitosan and heat treated chitosan samples at 80°C for 36, 48 and 60 hours.

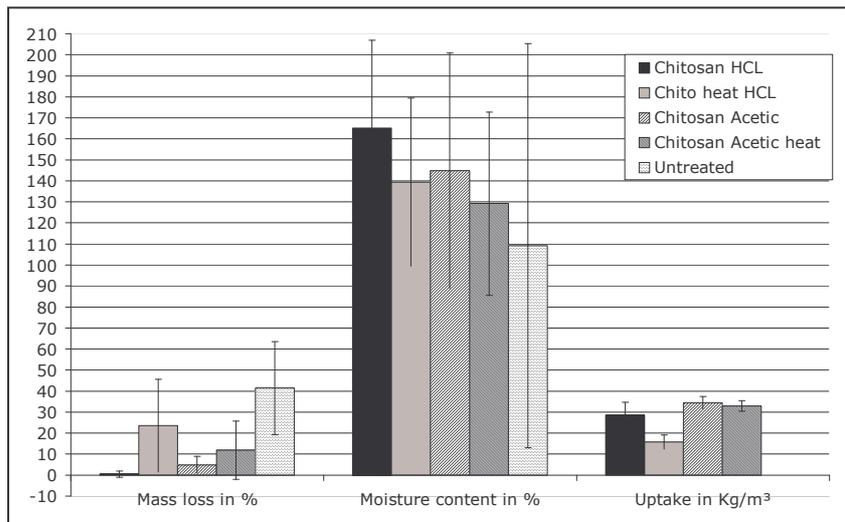


Figure 2: Antifungal properties of chitosan treated wood displayed as mass loss in %, moisture content in % and solution uptake of chitosan in Kg/m³. Pine samples exposed to *Coniophora puteana*

Anti-fungal properties

As seen in Figure 2, chitosan protonated with hydrochloric acid treated wood exhibits a mass loss of 0.46 % with a standard deviation of 1.46 % and n=18 and chitosan protonated with acetic acid had mass losses down to 4.91 % (st.dev 3.97 %, n=18). This shows that chitosan should be protonated with hydrochloric acid to achieve the best antifungal properties. The heat treated samples with hydrochloric acid protonated chitosan showed not so good results with a mass loss of 23.5 % (st.dev 22.08 %, n=18). The heat treated samples with acetic acid protonated chitosan showed a better effect with a mass loss of 11.87 % (st.dev 13.78 %, n=18). The moisture content of the samples was quite high and

according to the EN113 (1996) should moisture contents over 80% be rejected. This limit is at the time under international discussion if this should be changed to adapt to the new generation of wood preservatives. The untreated samples showed a very high mass loss of 41.4 % (st.dev 22.05 %, n=18). The heat treated chitosan protonated with hydrochloric acid shows a very high mass loss, although the non heat treated chitosan protonated with hydrochloric acid showed very good results. An explanation of this might be the low uptake of chitosan solution as displayed right in Figure 2. It is here clear to see that these samples only have the half amount of chitosan than the rest of the samples.

Mechanical properties

The samples tested for modulus of rupture (MOR) showed no significant changes within the wood species as seen in Figure 3. Pine gave an average MOR of 70 – 80 N/mm² and beech had an average MOR of 100 – 110 N/mm².

The modulus of elasticity (MOE) gave no significant change between the untreated samples and chitosan treated samples. The heat treated chitosan impregnated samples showed an increased MOE from 9773 N/mm² (st.dev 1453, n=30) of the untreated samples to a MOE of 12429 N/mm² (st.dev 1685, n=30). This gives an improvement of 27 % and is a statistical significant change.

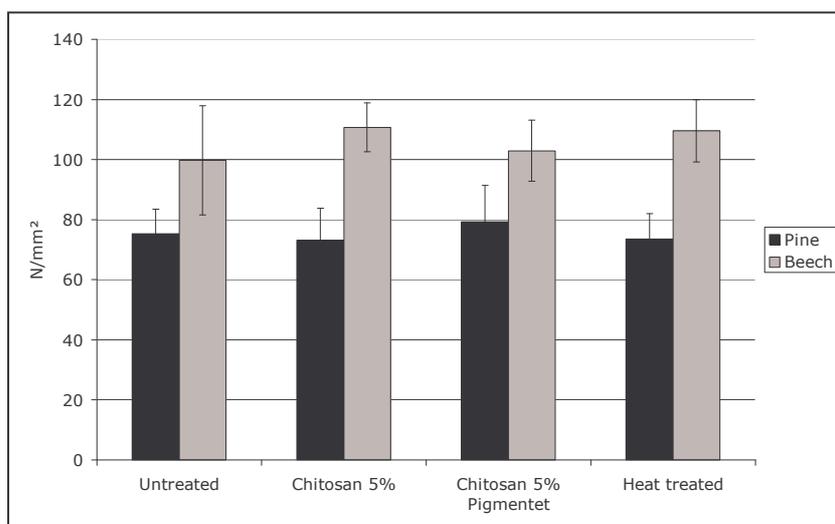


Figure 3: MOR of untreated, chitosan impregnated and heat treated chitosan samples of pine and beech displayed in N/mm². (error bars represent +/- 1 standard deviation, n=30)

CONCLUSIONS

Chitosan has for many years been internationally studied over several years and a lot of research is done in this field. To anaerobically heat chitosan treated wood one gets a new modified product that modifies wood. It is clear from these screening trials that heat treated chitosan has a possibility as a future wood preservative. Not only due to the brownish colour that is achieved, but with the right chitosan mixture, time and temperature it also enhances properties as hydrophobation, anti fungal properties and mechanical properties. There still has to be developed methods to describe what is happening under this

transformation in chitosan and wood when heated under anaerobe conditions. After the heating cycle, a distinct smell of acetic acid is present, both when hydrochloric acid and acetic acid was used. One hypothesis to describe this phenomenon is that the chitosan used in these trials have a degree of deacetylation of 80 %. This means that there is 80 % glucosamine and 20 % *N*-acetyl glucosamine in the solution. If the *N*-acetyl glucosamine is deacetylated by the process it would describe the acetic smell after the treatment. If this would be the case, it would enhance the antifungal properties. These tests shows that the heat treated chitosan impregnated samples gives a lower anti fungal activity than normal chitosan impregnated samples. This might be explained with the possible depolymerisation of hemicellulose caused by the acetic acid released in the process. This again would lower the mechanical properties, which is not the case. In the future trials, microscopic and chemical analytic tests will be performed to find the mode of action of this treatment.

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NATWOOD TECHNOLOGY – A MATERIAL THERMAL WOOD MODIFICATION

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Keywords: Tempered wood, wood impregnation, wood modification

ABSTRACT

The Natwood Technology improves the physical properties of wood and wooden composites. Wooden parts, which are treated with this method, show amazing properties. Even soft wood turns solid and resistant. At high temperatures, the wood even becomes thermoformable. That opens completely new fields of applications. The process uses a solvent-free system. A melted mixture of natural resin and wax is pressed into the wood matrix under the application of pressure. This pressing, so called *loading the wood*, is made in a pressure vessel. The loading substance permeates the wood. According to the loading conditions a so called loading gradient is obtained, which results in a higher concentration of loading substance on the outside than in the wood core. The depth of penetration of the loading substance depends on pressure and temperature conditions, as well as of residence time. The absorption of the loading substance also depends on the species used.

INTRODUCTION

Wood is the most widespread material in our known world. Wood has been used since antiquity. Human beings have always been in contact with wood. That is probably the reason why we find this material so attractive. Besides its positive properties, wood also has decided disadvantages in comparison with other materials like metal, ceramics or plastics:

- 1) Wood shows high swelling and shrinkage at changing humidity.
- 2) Swelling and shrinkage result in checks and fissures.
- 3) Most species of wood show low surface hardness.
- 4) Wood can be used as a nutrient by various organisms.
- 5) Wood, which is exposed to weathering, can degrade drastically.

In the 19th century mainly natural substances, like tar or vegetable oil, were used to improve the swelling and shrinkage properties. However, successes were limited as technical requirements were not available for pressure and temperature control.

During the 20th century substances were generally used, which were made available by the chemical industry, like monomers of plastics, which after entering the wooden matrix were transversely crosslinked by heat or ionising radiation. The fields of application of this so-called polymer wood are rather limited because of the high price, of the large-scale technology and of the loss of "naturalness". Pressure-impregnated wood is widespread. By means of this method, different chemical

substances were employed for the wood, which inhibit the growth of microorganisms for a longer period of time. But the raw materials used are controversial owing to their toxicity for higher organisms (mammals) and some substances have recently been prohibited in many countries. The physical properties remain unchanged.

Since approximately 1985, thermally tempered wood has been investigated intensively. An example of this technology was the 'charring' of piles, which was already practiced in ancient times. The piles were used for fences or for foundations of buildings. The known disadvantages, like the scorched smell, reduced mechanical properties and excessive discoloration have still not been eliminated sufficiently.

Natwood technology connects the scientific analyses of the 19th century to improve the properties of wood with natural substances with the technical progress of the 20th and 21st century. Besides, Natwood combines the advantages of thermally tempered wood with wood, which is then enhanced.

EXPERIMENTAL

Loading substance

The demands on the loading substance were high and varied. It should remain solid till 80°C at least, then melt quickly and show a high viscosity gradient. At approximately 135°C it should be so thinly-viscous, that it can penetrate the wood structure easily from all directions by excess pressure and spread well in the wood cavities. Natural resin does not show these properties to the desired extent. Natural resin has the unpleasant property of softening even at low temperatures and with a further increase of temperature it does not show a high viscosity gradient. Besides, natural resins are not oxidation resistant, get an intense darker colour at increased temperatures and create a sticky surface.

A modified kind of resin had to be found, which did not show these disadvantages. After intensive research work, it was clear that only the combination of modified natural resins with an additive showed the desired properties. The additive comes from the material group of waxes.

The loading substance represents a material mixture of modified natural resins and waxes. After melting, those two material groups enter into a close mixture, which cannot be separated even by frequent solidifying, melting and very strong heating. In addition, waxes are highly water resistant, thermally stable and cheap.

Species tested

The following species of wood were tested to determine whether they were load-bearing:

European: beech, birch, pine, oak, spruce, alder, fir, poplar, cherry tree, ash, maple
North American: Weymouth pine,
South American: eucalyptus
Southeast-Asian: rubber wood, Paulownia
Asian: birch

Australian: eucalyptus

The treatment of pine was selected as an example. With the know-how of a laboratory and a pilot plant unit a productions plant was built, which made it possible to load approximately 1.5 m³ of wood with a maximum length of 2.2 m in one go. For this purpose, a pressure vessel was constructed, so that resin melting can be used at a temperature of up to 140°C and a maximum pressure of 10 bar.

Processing conditions

For the melting temperature, a range from 120-140°C, a pressure from 2 to 6 bar and a residence time from 10 to 60 minutes was defined.

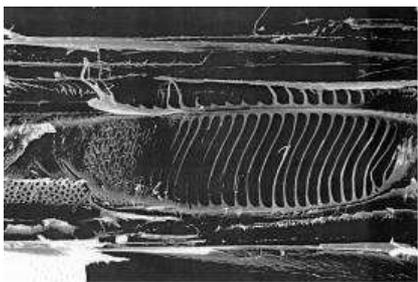
RESULTS AND DISCUSSION

Table 1 shows the influence of loading conditions on the loading gradient (percentage weight increase related to the untreated wood) for example birch with dimension of 550 x 160 x 20 mm³.

Table 1: Loading parameter

Pressure (bar)	Temperature (°C)	Time (min)	Loading gradient %
3	130	30	10
4	130	30	18
5	130	30	24
6	130	30	29

The loading gradient rises with increasing pressure and follows a square equation with a certainty degree of R² = 0.92. If higher loading gradients are required, the residence time has to be increased and possibly the temperature. But short times and low temperatures are more economical. The cavities are lined with the water repellent material and the cell walls coated with a quasi-protective layer (Figure 1).



Tests to improve surface hardness

Lamellae, with a dimension of 560 x 150 x 4 or 550 x 150 x 7 mm³ respectively of beech, pine, birch, oak and poplar were loaded. A 5 point determination per lamella was carried out before and after the treatment. The following Table 2 shows the average increase of hardness in percent.

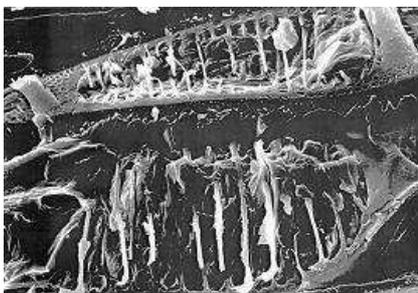


Table 2: Influence of loading on hardness

Wood species	Loading gradient	Increase of hardness %
beech	49	54
pine	73	156
birch	42	110
oak	20	56
poplar	66	64

The absorptive capacity of the types of wood is very varied, because of their anatomy – some timbers can absorb more than their net weight. However the absorptive capacity can be well adjusted by the machine settings. For reasons of expense and time it is recommended to work

Figure 1: Electron micrograph of birch (x 1000)

with a loading gradient in the range of 20 to 30 %, where the properties are already improved sufficiently.

Examination for dimensional stability

Pine boards of different dimension were stored for 4 weeks at 20°C and 65 % relative humidity (RH). and afterwards loaded with a resin-wax mixture at 135°C at different pressure. The results were loading gradients of 7 to 60 %. Those boards were stored together with untreated boards of the same dimension in the conditioning cabinet for 450 days. The RH was constantly changed from 35 % to 85 % and back. One cycle took 110 days on average. The samples were weekly examined for changes in weight and dimension. The relative change in weight and in thickness is shown in the following examples (Figure 2 and 3).

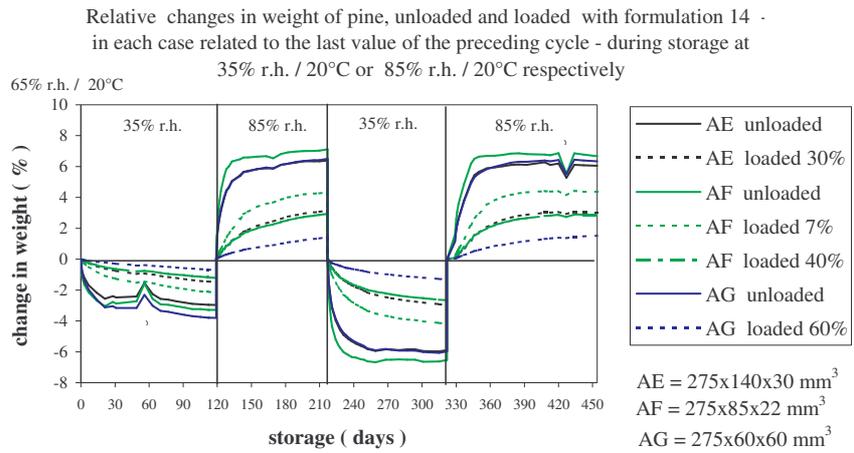


Figure 2: Influence of humidity on change in weight

The influence of the loading gradients can be clearly seen, although the effects at 30 and 40 % are very similar. This is also the range where the process works most economically. On the untreated boards can be seen the natural influences on the dimension, which is covered on the treated boards. The variations in thickness of untreated wood are dramatic anyway and can be reduced by treatment.

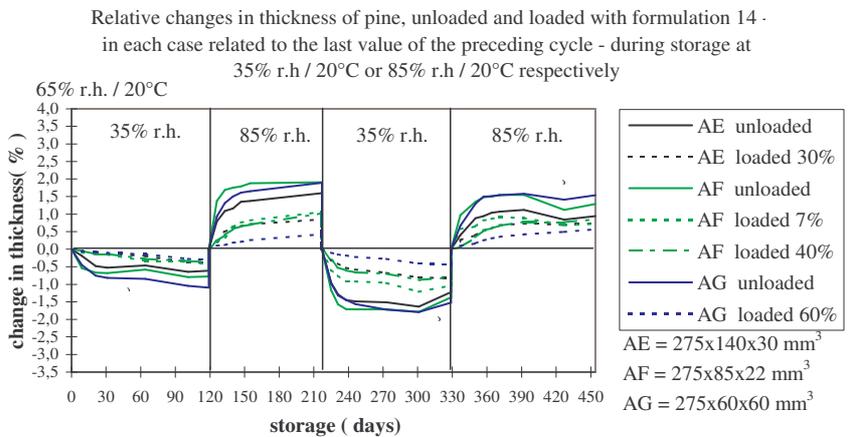


Figure 3: Influence of humidity on change in thickness



Figure 4: After 5 months weathering

Tests on the influence of outdoor exposure

Since there is a renewed demand for wooden facades, it was decided to test the level of stability outdoors. For that purpose new mixtures with UV-stabiliser or fungicide respectively were created besides the standard formulation. The difficulty was to find a commercial preparation which is compatible with our resin/wax-mixture and resists the loading conditions. Ultimately two products could be found, which were resistant against high temperatures and showed good effectiveness. The photo attached shows pine boards treated with different formulations in comparison with untreated wood. The boards were exposed to the weathering at 45° angles to the south at the beginning of March.

The untreated parts were heavily overgrown with mould and had developed severe checks. At the treated boards there were differences according to the formulation. But some seemed to be like new. However after a further six months the difference between the mixtures was levelled. A light greying appeared, but the development of checks could be neglected. The most attractive boards were those which had received an addition coating of glaze in addition to the loading. Some of the untreated boards were so severely split, that parts dropped off.

Termite resistance tests

In many countries termites are a real problem. We were interested if wood, which is treated according to our method, showed a higher resistance. Pine wood with an average loading gradient of 26 % with the standard formulation was investigated according to EN 118. Termite attack is judged on a scale in four parts. 5 of 6 samples were in class 1, one sample was class 2. The untreated samples were class 4, which means they were perforated. The examination was carried out by CTBA in Bordeaux.

Fire resistance tests

Oak, pine, beech and spruce were loaded with standard formulation. The tests for B2 (flammable) flammability classification proved that this level could be achieved without problems. Due to requests, classification B1 (flame retardant) was also investigated. This could only be obtained with oak after developing a special loading formulation. The tests were carried out by TGM in Vienna.

Bending strength tests

Within the scope of Mr. Rudolph's dissertation at Rosenheim College loaded pine samples were compared with other treated wood parts. The loaded pine samples achieved the best results of coniferous wood. The standard values were exceeded more than twice.

Tests to improve durability

In a research project at Rosenheim College, it was determined, that loaded pine samples can be assigned to durability classification 3. Durability could be improved by 2 classes compared with unloaded pine. Wooden parts tempered with Natwood-technology can be used in hazard classification 3 (weathering without soil contact).

Examination for tempering wood composites

3-ply solid wood boards, veneer hard boards (Multiplex boards) and thermo-wood were tempered with the Natwood-technology for tests in combination with use as wooden facades. The examinations are still

being carried out. The loading could be performed without any problems. As was expected - the loading gradient was high, the glue joints were not affected. The tempering of the board's front with the open conductive vessels, which are extremely stressed by weathering, was carried out very accurately. At the time of loading the boards must already have their final dimensions to use the advantage of the special loading of the front side of the boards. Changes in dimension due to loading were not determined.

CONCLUSIONS

The product and process name of the method introduced is Natwood®. In the development work of Natwood the objective was to carry out a modification of wood with mainly natural substances to adapt the properties of European wood species to rare tropical wood species. This goal was reached with a combination of material and moderate thermal treatment. The advantages of Natwood tempered wood are:

- Improved swelling and shrinking behaviour
- A reduction in the development of checks and fissures
- An improvement in surface hardness
- An improved coating adhesion
- Increased resistance against attack by different organisms

With the help of Natwood-technology the resistance of wood against outdoor weathering – concerning greying and formation of fissures – can be improved. By the improved swelling and shrinking behaviour and by the reduction in fissures and checks the quality of surface treatment increases, lacquers do not come off, the period for repainting is extended. The disadvantages of Natwood tempered wood are:

- Natwood products only show a little better flammability in comparison with untreated natural wood.
- In certain applications you have to counteract this drawback with flame retardants. A Natwood-tempered oak flooring with a thickness of 10mm reaches flammability classification B1.

ACKNOWLEDGEMENTS

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ENZYMATIC COUPLING OF PHENOLIC COMPOUNDS ONTO WOOD: OPTIMIZATION USING RADIOISOTOPE LABELLING

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Keywords: Laccase; enzymes; fiber modification; wood modification; radioisotope labelling, solid state NMR

ABSTRACT

Wood fibers and particles as well as solid wood may be chemically modified by grafting (*i.e.*, covalent coupling) of phenolic compounds onto wood lignin using oxidative enzymes such as laccase as catalysts. Such phenolic compounds may carry functional groups in order to improve the strength properties of paper or wood composites. Here we have used ¹⁴C and ¹⁵N labelled 4-hydroxy-3-methoxybenzylamine (HMBA) as model compounds to investigate the grafting process by mass balance analysis and solid state NMR. ¹⁴C mass balance analysis proved to be an efficient and reliable method to optimise grafting reactions directly on any type of woody material. Essential process parameters such as laccase and phenol dosages, solid to liquid ratio, treatment time, temperature and pH could be optimised to achieve grafting yields of nearly more than 90 %. Furthermore, the presence of HMBA on the modified wood was confirmed by solid state ¹⁵N-NMR. Using milled wood lignin (MWL), laccase catalysed coupling of HMBA to lignin was demonstrated by molecular weight distribution analysis using gel permeation chromatography and subsequent radiochemical detection.

INTRODUCTION

Laccase, a blue multicopper oxidase, is a widespread enzyme primarily produced by wood rotting fungi. It has a broad substrate range and catalyses the oxidation of large variety of monomeric as well as polymeric phenols and aromatic amines to free radicals with concomitant reduction of dioxygen to water. The use of dioxygen as the oxidant, its relatively high stability as well as its commercial availability make this enzyme an ideal candidate for industrial applications. Recently, the use of laccase for the modification of wood fibres has received considerable attention. For example, laccase has been shown to greatly improve the internal bond of fibre boards (Felby *et al.* 2002). This effect may be explained by the fact the laccase oxidizes the phenolic structures in wood lignin creating relatively stable free radicals that may participate in fibre bonding by subsequent radical coupling. Laccase may also be used to improve the mechanical strength of paper and wood products by so-called enzymatic grafting of low molecular weight compounds carrying suitable functional groups onto lignin (Chandra and Ragauskas 2002, Hill and Çetin 2000, Hüttermann *et al.* 2001, Pedersen *et al.* 1997). Common analytical methods, such as UV/VIS and IR spectroscopy, HPLC and wet chemical analysis have not yet

proven very suitable for the analysis of the grafting mechanisms and the optimisation of reaction conditions. The reason for these analytical problems is the inhomogeneous nature of the wood matrix and particularly lignin strongly interferes with the detection of grafting compounds, when wood or isolated lignin is used as the substrate. One possibility to get more information on the grafting process is the use of isotope labelled grafting compounds that can easily be detected and quantified in complex reaction mixtures containing lignin. Here we have prepared and investigated one such compounds, 4-hydroxy-3-methoxybenzylamine, which was labelled with ^{14}C or ^{15}N for laccase catalysed grafting onto lignin. This compound contains an amino group that, once grafted onto wood fibres, may crosslink with aminoplasts thus increasing bonding strength.

EXPERIMENTAL

Enzymes

A recombinant laccase from *Trametes villosa* (product no. 44008) was obtained from Novo Nordisc and used for all experiments. Laccase activity was measured spectrophotometrically at 420 nm using 0.4 mM ABTS as a substrate ($\epsilon = 43.2 \text{ cm}^2/\mu\text{mol}$) in 20mM sodium succinate buffer (pH 5). One unit of laccase activity was defined as the amount of enzyme required to oxidize $1 \mu\text{mol ABTS min}^{-1}$ at 30°C .

Preparation of milled wood lignin (MWL)

Crude MWL from loblolly pine was fractionated by GPC on LH20 (see below) and the high molecular weight fractions eluting at 35-65 ml were combined and used in the experiments. Partially methylated MWL was prepared by stirring 30 mg high molecular weight MWL with 42 mg K_2CO_3 and $40 \mu\text{l CH}_3\text{I}$ in 1.4 ml dry dimethylformamide (DMF) in the dark for 72 h at room temperature. The reaction mixture was dissolved in 20 ml ethyl acetate which was washed with 20 ml saturated brine. The organic phase was dried over NaSO_4 , the solvent rotary evaporated to dryness, and the MWL residue dissolved in $150 \mu\text{l DMF}$.

Synthesis of [^{14}C] and [^{15}N]4-hydroxy-3-methoxybenzylamine

[^{14}C]4-hydroxy-3-methoxybenzylamine (^{14}C -HMBA) was synthesized as described by Kaga *et al.* (1989) from ammonium formiate and [^{14}C]vanillin (obtained from ARC; labeled at the carbonyl carbon at a specific radioactivity of 55 mCi/mmol) with the following modifications. To remove inorganic impurities, ^{14}C -HMBA was extracted with ethyl acetate prior the hydrochlorination step. Then the amine was separated from byproducts by TLC (Silica gel 60 F₂₅₄ (VWR); eluent 85% chloroform/15 % methanol). ^{14}C -HMBA was extracted from silica gel with methanol and its structure and purity (chemical and radiochemical) was confirmed by NMR (^1H and ^{13}C) and HPLC (Agilent 1100), respectively. [^{15}N]4-hydroxy-3-methoxybenzylamine (^{15}N -HMBA) was synthesized starting from 2.5 g [^{15}N]ammonium hydroxide (3.3 N, Cambridge Isotope Laboratories, Inc.) which was neutralized with 500 mg (10.9 mmol) concentrated formic acid (98 %). After cooling down, the solvent was evaporated and the labeled ammonium formiate (0.5 g) obtained as white crystals which were reacted with vanillin as described above yielding 50 % ^{15}N -HMBA. The product was purified by recrystallisation from ethanol and its purity was confirmed by HPLC and solid state NMR.

Radiochemical analysis

Samples (solid and liquid) were mixed with scintillation cocktail (Optiphase HiSafe3, Wallac) in a suitable ratio and counted for 5 minutes on a Wallac 1409 liquid scintillation counter (LSC).

Enzymatic grafting

150 mg spruce wood particles (size 0.2-2 mm) were placed in a 4 ml glass vial to which the grafting solution was added at a solid/liquid ratio of 1:20 based on wood dry weight. The final concentrations of ingredients in the liquid phase were 0.1 U/ml laccase and 2 mM ^{14}C -HMBA in 5 mM acetate buffer at pH 5.0 under various conditions. The reactions were vigorously shaken for various times up to 120 hours. In other reactions the wood particles were incubated at a solid/liquid ratio of 1:2 (*i.e.*, 200 % moisture content) in which the final concentrations were 0.1 U/ml laccase, 20 mM ^{14}C -HMBA or 20 mM ^{15}N -HMBA in 5 mM acetate buffer at pH 5.0. After incubation the reaction mixtures were centrifuged and the pellets washed several times with water. All fractions were collected, counted by LSC and the data used for mass balance analysis. Grafting yields were calculated as the sum of radioactivity remaining in the supernatant and washing steps. Reactions with ^{15}N -HMBA were performed for 24 h at a solid/liquid ratio of 1:2 as described above. The treated wood particles were washed and the pH adjusted to ~8. The dried wood particles were subjected to NMR analysis as described below. Grafting reactions for GPC (see below) were performed as above with the exception that MWL was used instead of spruce wood particles. MWL reactions contained 0.2 U/ml Laccase, 1 mM ^{14}C -HMBA and 8 mg/ml MWL suspended in 50 mM acetate at pH 5.0 and were incubated for 2 h. Then the reactions were centrifuged, the supernatant removed and the MWL pellet washed several times with water. The aqueous supernatant was diluted in DMF at a ratio of 1:30 (v/v), and the MWL pellet was dissolved in DMF before GPC analysis.

Gel permeation chromatography (GPC)

Columns (1.8 x 40 cm) of Sephadex LH-20 (Amersham Biosciences) were prepared in DMF with 0.095 mM LiCl for analysis of grafting reactions and without LiCl for fractionation of MWL. Samples (5 ml) were loaded onto the column, eluted with DMF/LiCl, collected using a fraction collector and the fractions analyzed by radiochemical detection. Typical recoveries were 95-98% of the total radioactivity initially added to the reactions.

NMR analysis

Solid-state ^{15}N -NMR spectra were recorded on a Bruker Avance 300 spectrometer (standard bore), equipped with a 4mm broad band MAS probe head. The rotational speed for all experiments was 6 kHz. Ramped ^{15}N -CP/MAS spectra (cross polarization with magic angle spinning) were measured with a Bruker standard pulse program and referenced relative to $^{15}\text{NH}_4\text{Cl}$ (= 0 ppm).

RESULTS AND DISCUSSION

Enzymatic grafting on milled wood lignin (MWL)

To demonstrate that laccase is able to bind ^{14}C -HMBA to lignin during the grafting process, a water insoluble, high molecular weight MWL was chosen as a lignin model substance to be able to follow the reactions by GPC. Figure 1 shows the molecular weight distribution of radiolabel in reactions containing ^{14}C -HMBA, MWL and laccase including controls without laccase. In the presence of laccase, about one half of the radiolabel was found in the water insoluble MWL pellet, whereas the other half remained in the supernatant. In the chromatogram of the supernatant most of the ^{14}C eluted at the molecular weight of monomeric HMBA with some ^{14}C eluting at higher molecular weights indicating that some of the HMBA had polymerised but remained water soluble. In control reactions without laccase, no significant radiolabel was found in the MWL pellet and all of the ^{14}C -HMBA was recovered in the supernatant.

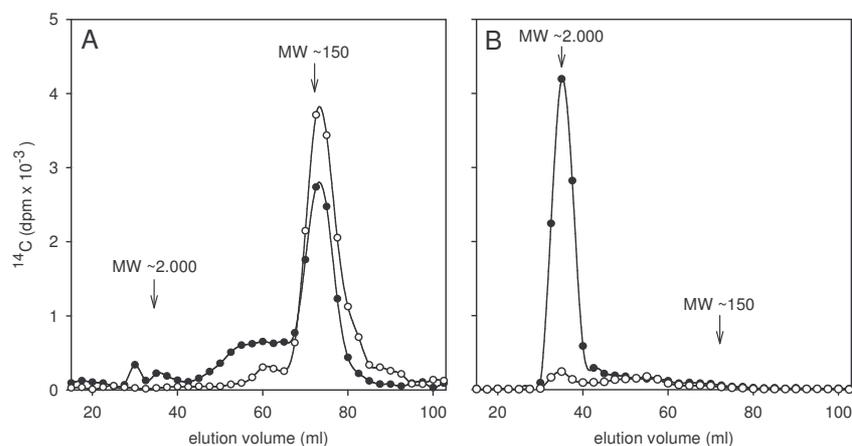


Figure 1: Molecular weight distribution of ^{14}C in the presence of ^{14}C -HMBA, MWL and laccase (●) and of controls without laccase (○) after 120 min reaction time. (A) supernatant, and (B) insoluble MWL pellet

The chromatography was done in DMF containing LiCl indicating a strong and possibly covalent binding of ^{14}C -HMBA to MWL by laccase. However, the amount of water soluble, polymerised HMBA in the supernatant varied depending on the reaction conditions (data not shown). Under less favourable conditions a shift in the molecular weight distribution to higher molecular weights as well as lower grafting yields were observed. Therefore, GPC analysis of MWL using radiolabeled grafting compounds may serve as a tool to examine and optimize grafting reactions.

Enzymatic grafting on spruce wood particles

Figure 2 shows temperature and pH profiles of grafting reactions performed at a solid to liquid ratio of 1:20. The pH optimum in buffered grafting reactions was 5 and thus close to the pH optimum of laccase activity (Figure 2A). The slight increase in grafting yield from pH 7 to pH 8 may be due to the presence of the deprotonated form of HMBA under alkaline conditions. However, the non-buffered reaction with an initial pH value of 7 gave the same grafting yield as the reaction

buffered at pH 5 (single data point in graph). The pH of the reaction mixture including wood particles before and after the reaction was found to be approximately 5 and thus the result was due to the presence of wood. It appears that the buffering capacity of wood itself is sufficient to maintain a fairly constant pH throughout the grafting reaction. The grafting yields obtained at 30°C and 50°C were about the same (Figure 2B). However, at 70°C the yields dropped significantly probably due to enzyme inactivation or increased side reactions such as self-polymerization and/or quinone formation. The binding rate was not linear and most of the HMBA was bound during the first 60 minutes.

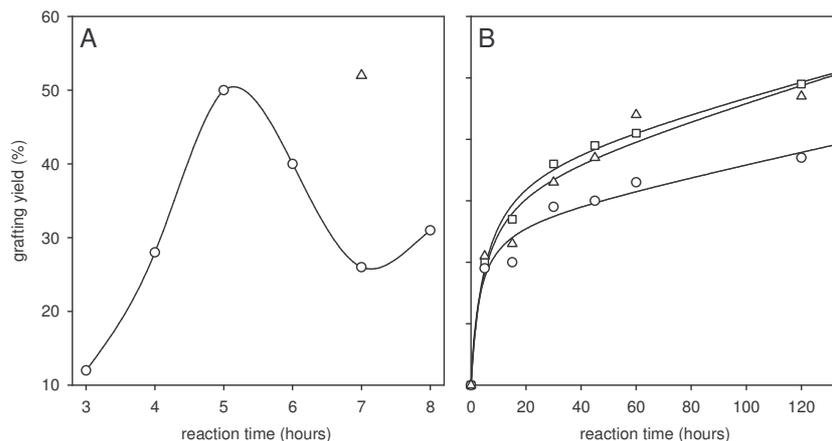


Figure 2: pH (A) and temperature (B) dependence of grafting yields of ^{14}C -HMBA on spruce wood particles at a solid/liquid ratio of 1:20. (A) 30°C (\square), 50°C (\circ), 70°C (\triangle); (B) 50 mM acetate buffer (\circ), no buffer at pH 7.0 (\triangle)

Table 1 shows that grafting yields obtained with ^{14}C -HMBA on wood particles strongly depended on the solid/liquid ratio. Reactions done in suspension (ratio 1:20) leveled off at a grafting yield of less than 50 %, whereas grafting yields of up to 96 % were obtained when the amount of liquid was kept low (ratio 1:2, *i.e.*, 200 % moisture content based on wood dry weight). Low grafting yields at high liquid/solid ratios may be due to extensive side reactions of the reactive radical intermediates formed by laccase leading to dead end products such as quinones and polymers. Such unwanted reactions may be less pronounced low liquid/solid ratios, where these intermediates are in close contact with wood and therefore have a higher probability to bind to it.

Table 1: Grafting yields at different solid/liquid ratios and incubation times

Liquid/solid ratio	^{14}C -HMBA (mM)	Reaction time (h) at 30°C	Bound ^{14}C (%)
20:1	2	3	46
20:1	2	72	48
2:1	20	4	52
2:1	20	24	88
2:1	20	72	96

Solid state NMR analysis

Since ^{14}C labeling gives no information on chemical changes to the functional amino group of HMBA that may have occurred during grafting, solid state ^{15}N -NMR was employed. To obtain a detectable signal on treated wood particles, HMBA was labeled with ^{15}N . The signal

at 53.3 ppm (Figure 3) is indicative of an amino group demonstrating that it remained intact after grafting. No signal was observed in the absence of ^{15}N -HMBA (not shown).

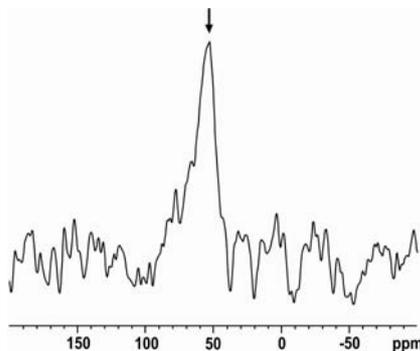


Figure 3: Solid state ^{15}N -NMR spectrum of spruce wood particles treated with ^{15}N -HMBA and laccase.

CONCLUSIONS

Our investigations showed that the use of radiolabeled grafting monomers is a feasible way to control and optimize grafting reactions. The separate analysis of the solid wood particles and corresponding supernatants of the reactions allowed for simple mass analysis, which helped to obtain valuable information about the efficiency of the process. The facile quantification of compounds grafted onto the lignin suggests possible further applications of radiolabeled chemicals for a rapid modification and optimization of various reaction parameters such as pH, temperature, incubation time, concentrations of reactants etc. GPC and NMR as more specific analytical tools provide more detailed information and further possibilities for controlling grafting reactions. However, GPC utilizes milled wood lignin instead of a native lignocellulose matrix.

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CHANGES IN MECHANICAL PROPERTIES OF FURFURYLATED WOOD

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Keywords: Applications, furfurylation, impact bending, hydrolysis, modified wood, Scots pine

ABSTRACT

Modification of wood will, in any perspective, lead to mechanical and physical changes of the material. The search for enhanced wood products and the ability to use wood in new applications are driving forces for research in this field. Mechanical and physical properties and resistance to fungal decay are often improved. However, impact bending is normally reduced by chemical modification of wood. A promising method of wood modification is the furfurylation process. Major improvements have been seen for decay resistance, dimensional stability and to some extent; stiffness, hardness and modulus of rupture. However, impact bending strength has been found to decrease due to the treatment. Furfurylation of wood is a modification method which involves reaction with furfuryl alcohol under weak acidic conditions at elevated temperatures. The change in impact strength properties could originate from both cross-linking and hydrolysis of cell wall constituents. Furfurylated softwood products have been on the market for about 2 years from a commercial production plant. The demand for such wood for cladding, decking and roofing is constantly increasing, although these applications are examples where impact strength is of minor importance. In addition, results from a study where furfurylated wood was subjected to accelerated climatic ageing is presented. The aging experiments were accelerated by exposing the wood samples to 80°C and 100 % relative humidity for 10, 28 and 38 days. There was a significant reduction of impact bending due to treatment, and a trend towards a minor reduction due to the exposure, which however was not statistically significant. Furfurylated sapwood of Scots pine (*Pinus sylvestris*) had a reduction of impact bending strength in the range 19-37 % with an average of 24 %.

INTRODUCTION

The search for improved wood products and the ability to use wood in new applications are driving forces for research in the field of wood modification. Mechanical and physical properties, and resistance to fungal decay are often improved by wood modification processes. However, impact bending is normally reduced by these processes.

The use of furfuryl alcohol (FA) as a wood modification agent has been known for some decades. (Goldstein 1955, Goldstein 1960, Goldstein and Dreher 1960, Anaya *et al.* 1984, Amaury *et al.* 1988). In the 1990s, Schneider (1995) and Westin *et al.* (1996) simultaneously developed new catalytic systems for furfurylation of wood. These new systems resulted in relatively cheap manufacturing processes for furfurylated wood with

good properties with respect to mechanical strength, stability and decay resistance.

It is well understood that heat-treatment and even high temperature drying have negative effects on strength properties of wood depending on temperature, humidity and time (Salamon 1963, Salamon 1969, Thermowood Handbook: Anonymous 2003). Thermal degradation is explained by acid catalysed hydrolysis, and the degradation rate is higher in humid conditions at elevated temperatures and closed systems where acids formed build up in higher concentration than in open systems under ambient conditions (Stamm 1956).

Strength loss of wood has also been observed for fire retardant treated wood. A study on the long-term effect of fire retardants on bending strength found a strong influence by pH and dissociation constant on the loss of strength properties MOR (Modulus of Rupture) and MOE (Modulus of Elasticity) [Lebow and Winandy 1999]. Strength loss was then studied at elevated temperature (66°C, 75 % relative humidity) over 4 years. Data was used to predict strength loss for a period of 10 years. A product containing Guanylurea phosphate/boric acid had a pH of 3.13 in wood and a dissociation constant of 7.9×10^{-8} . This was reported to give 10 % strength loss and a known trouble-free service life of more than 15 years (Lebow and Winandy 1999).

Winandy (2001) reported in a review article that FR (Fire Retardancy) treatments reduce the initial strength of wood. Parts of this reduction occurred in the re-drying after impregnation. It is also concluded that the key factor of thermally-induced strength loss are FR retention and wood moisture content. When both increase, wood degradation also increases (Winandy 2001).

One of the promising methods of wood modification is the furfurylation process. Major improvements have been seen for decay resistance (Lande *et al.* 2004), dimensional stability and to some extent: hardness, MOE and MOR. Impact bending strength has been found to decrease due to such treatment (Epmeier *et al.* 2004). When producing furfurylated wood, the wood is exposed to elevated temperatures at high moisture content with an acidic catalyst system for polymerisation of furfuryl alcohol. These are all factors that could influence the strength properties of produced materials both during production and later in use. Both cross-linking and hydrolysis of cell wall constituents can contribute to this effect. It is therefore of great importance to understand the reduction in strength properties on a short time basis and on a long time basis.

Furfurylated softwood products have been on the market for about two years from a commercial production plant. The demand for such wood for cladding, decking and roofing is constantly increasing and several buildings are now covered by these products. Although the applications mentioned are examples of use where impact strength is of minor importance, it is important to clarify the long-term strength properties for use in new products. The work done in this paper is the first step in documenting the reduction in impact bending strength of furfurylated wood materials.

EXPERIMENTAL

Wood material

Wood materials were selected from a stock of Scots pine (*Pinus sylvestris*) boards that had good uptake during impregnation. A total of 530 samples were machined to 20 x 20 x 300 mm³. An end-matched sample was used to determine the moisture content gravimetrically after drying at 103°C for 18 hours. Samples with any defects or visible heartwood were rejected. The samples were randomly divided into three groups of 120 samples each. One group was used for untreated control and the other two groups were treated within the laboratory by the furfurylation process (Lab 1 and Lab 2).

In addition, 100 samples were taken from virgin VisorWood (furfurylated Scots pine) in stock at Kebony Products and 56 samples were taken from naturally weathered cladding materials produced at Kebony Products (Porsgrunn, Norway). These materials were included in the testing for comparison. The samples were machined to 15 x 15 x 300 mm³ due to limited dimensions of the cladding boards in stock.

Treatment

Laboratory treatments were done by a standard VisorWood formulation mixed and prepared for this experiment (Lab 1) and an experimental formulation with changes in the catalyst system for polymerisation (Lab 2).

Impregnation procedure was vacuum at 0.1 bar for 45 min and pressure at 8 bar for 90 min. Table 1 summarises moisture content at treatment, retention of treatment liquid and Weight percent gain (WPG) obtained by the treatment. VisorWood materials were cut from standard cladding boards and no data on moisture and uptake was available for the specific samples. Reported WPG is an average of produced WPG at Kebony Products factory when using Scots pine sapwood and a Visorwood-40 formulation. Curing for both lab-work and VisorWood was done by using steam at 100°C for 8 hours.

Table 2: Moisture content, retention and weight percent gain of treated material

Material	MC %		Solution uptake		WPG	
	before treatment		% of dry mass		% of dry mass	
Untreated Scots pine	13.6 %	(±1.6)				
Scots pine Lab 1	13.1 %	(±1.8)	160 %	(±46.0)	31.9 %	(±9.7)
Scots pine Lab 2	13.5 %	(±1.5)	163 %	(±40.1)	23.7 %	(±6.3)
VisorWood (Scots Pine)					30 %*	
VisorWood - weathered					30 %*	

*Average value from KP production using the Visorwood-40 formula

Accelerated ageing and natural weathering of wood samples

The laboratory samples (Lab 1, Lab 2 and Untreated samples) were randomly divided into four groups of 30 samples each. The VisorWood samples were divided into two groups of 50 samples. One subset was stored at ambient temperature and humidity. The remaining samples were placed in sealed plastic containers with free water present to ensure 100 % relative humidity. The containers were then placed in an oven at 80°C for 10, 24 and 38 days (Table). After each exposure period

the samples were dried to 0 % MC prior to impact bending testing. Naturally weathered cladding boards were exposed vertically facing south for a period of 10 months (August -03 to June -04).

Table 2: Labelling and time of exposure of the grouped species

Material	Unexposed	Exposure: 80°C 100 % relative humidity		
	0 days	10 days	24 days	38 days
Untreated Scots pine	U-to	U-t1	U-t2	U-t3
Scots pine Lab 1	L1-to	L1-t1	L1-t2	L1-t3
Scots pine Lab 2	L2-to	L2-t1	L2-t2	L2-t3
VisorWood (Scots Pine)	V-to	V-t1		
VisorWood - weathered		Exposed 10 months		

Impact bending

The measurement of impact bending strength was performed in a pendulum machine. The maximum energy for the test rig was set to 50 Joule for the samples of 20 x 20 mm cross section, and 15 Joule for the samples of 15 x 15 mm cross section. The work load to failure was recorded with an accuracy of +/- 0.5 Joule. The results were reported as kJ m^{-2} by using Eqn. 1

$$A_w = (1000 \times Q) / (w \times h) \quad (1)$$

where Q is work in Joule, and w x h is the cross section in mm^2 .

RESULTS AND DISCUSSION

The results from the impact bending experiments are shown in Figure 1. The untreated control samples (U) had an average value of impact bending of slightly above 37 kJ m^{-2} for all exposure times, except after 28 days. The higher results after 28 days of weathering exposure must be considered as an artefact of the random distribution of samples between the groups. Average impact bending strength of Scots pine is reported to be 36 kJ m^{-2} (Tretknisk Håndbok, 1999). The variation in impact bending is fairly equal for each group in the test. For the furfurylated samples, the general trend shows a decrease in impact bending strength for the first exposure times and then seems to level off. The 80°C temperature was chosen to give a high stress level to be able to detect changes within reasonable time of exposure.

The furfurylated samples L1, L2 and V all show a considerably lower impact bending strength than untreated samples. However, the difference is not statistically significant due to the large variation in each group. However, the fairly equal variation in the impact bending strength results in all groups indicates that the reduction in impact bending strength can be predicted with a suitable model.

The L2 solution had a simpler catalytic system than solution L1, containing only one carboxylic acid and a higher pH of 4.3 compared to pH 3.7 for solution L1. The polymerisation of furfuryl alcohol in wood is inversely proportional to pH; the lower the pH, the higher the polymerisation rate. Both L1 and L2 had the same retention of liquid but resulted in two different WPG, 32 % and 24 % respectively. Furfuryl alcohol has a boiling point of 171°C, but in the presence of water they form an azeotrope with a boiling point of 98.5°C. The lower conversion rate of furfuryl alcohol to poly-FA in L2 results in a lower WPG after curing due to this azeotropic distillation of FA and water. This might explain the lower WPG and higher loss of FA during polymerisation. However, the slightly higher pH for L2 than L1 may also contribute to the

smaller reduction in impact bending strength for L2 compared to L1. The decrease in impact bending can thereby be explained by different pH levels during exposure to elevated temperature under humid conditions, but also the difference in WPG. The presence of cross linked poly-FA in wood will by itself have a negative effect on impact bending. However, MOE and MOR do not decrease due to the furfurylation process (Epmeier *et al.* 2004).

The L1 samples were very similar to the results from the Visorwood samples (V) for unexposed samples and samples that had been exposed for 10 days at 80°C and 100 % RH. Weathered Visorwood also had the same impact bending strength. This indicates that the small differences in the production of the samples between laboratory and factory do not influence this property and that natural weathering for 10 months does not contribute to further degradation.

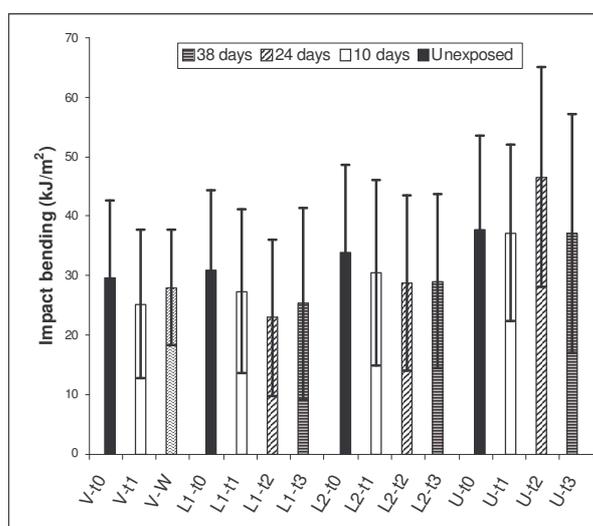


Figure 1: Impact bending of wood samples after artificial weathering at 80°C and 100 % relative humidity for 0 days (t0, reference), 10 (t1), 24 (t2) and 38 (t3) days. (V = Visorwood [Scots Pine], V-W = Visorwood weathered, L1=Laboratory treated Scots pine samples [1], L2=Laboratory treated Scots pine samples [2], U=Untreated Scots pine)

CONCLUSIONS

Furfurylation of wood reduces impact bending strength. Most of the reduction takes place during the production of the material. However, elevated temperatures and humidity further reduces impact strength over time. The results from this trial cannot be used to predict the change in the impact bending strength in the long run, but the results indicate the impact of a worst case scenario. Further studies are needed to fully describe the long term effect of the furfuryl treatment on the impact bending strength of these materials. Impact bending strength for furfurylated wood in this study decreased by 35 % for materials with an average of 32 % WPG and exposed to 80°C and 100 % RH for 38 days.

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PROPERTIES OF MODIFIED WOOD COATED WITH DIFFERENT STAINS

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Keywords: acetylation; DMDHEU; glue; heat treatment; interlace treatment; melamine; modification; paint; surface; window frame

ABSTRACT

In Germany the usage of wood for window frames has decreased dramatically during the last decade, because of the high maintenance costs due to low natural durability and low dimensional stability of European wood species. In a joint project of several German research institutes and the industrial window manufactures, the following wood modification systems were compared:

- heat treatment (3 different materials from 2 companies)
- acetylation (pine sapwood and beech wood acetylated with acetic anhydride)
- polymerisation (melamine resin treated pine sapwood, interlace treatment)
- wax treatment (pine sapwood, impregnated with natural resin and waxes)

Material properties such as moisture content, dimensional stability, capillary water uptake, durability and behaviour of coatings on modified wood were investigated. After artificial weathering, several surface properties, such as cracking, flaking and discoloration were evaluated on samples coated with different stains. The results show, that by a proper combination of modified wood together with an optimal coating system a long time durable material is provided.

INTRODUCTION

The usage of wood for window frames in Germany has decreased dramatically during the last decades. The reason is the high maintenance costs due to the low natural durability and low water resistance of European wood species. The market share of wooden window frames in Germany is below 20% nowadays. Most of the end users would prefer wooden window frames, but they are not willing to do the necessary maintenance work (Lechner 2003). Therefore, consumers nowadays prefer window frames made from plastics or metals. The plastic and metal window frame industries try to imitate wood window frames since the customers prefer a wooden optic in their living area.

The main benefit of plastic and metal windows is the longer service intervals. Whereas wooden window frames need to be maintained every 2-3 years, plastic and metal window frames require to be renovated only every 8-10 years. There are various reasons for such short maintenance intervals. As long as the coating is undamaged, the window frame stays intact. The coating of a wooden window frame may be damaged through mechanical influence, UV-light, or water. Water may gain access to the wood via small grooves or cracks (as joints in the corners).

The change of moisture content in the window frame leads to swelling and shrinking of wood. This creates new grooves and broadens existing grooves. Subsequently, more water is able to access the wood. Eventually, water detaches the coating from the wood and gives microorganisms a chance to grow. The goal of the window frame industry is to reduce the water uptake of the material and to reduce the further effects caused by the water in wood (Schmid 2003).

In a joint project of several German research institutes and the industrial window manufactures, several novel wood modification systems were compared. The aim of this project was to investigate the properties of modified woods which are already sold on the market or could soon become available.

This investigation consists of the following steps:

- investigation of basic material properties such as dimensional stability, durability and mechanical properties
- investigation of processing-related properties such as paint behaviour and glueability.

The information on the basic material properties, which are based on the influence of water, was already published (Krause *et al.* 2004). The investigation was done to achieve several objectives. One aim was to show differences between untreated and modified wood with regard to general coating performance. A further aim was to show differences between the modification systems.

EXPERIMENTAL

All modified wood was produced in industrial or pilot plant processes. Samples of untreated wood and differently modified wood (Table 1) were processed to obtain a size of 150 ± 2 mm length, 74 ± 1 mm width and 18 ± 1 mm thickness. The surface of wood was planed before coating.

Table 1 Overview of investigated wood material.

	Material	lat. Name	Abbre-viation	Literature
untreated wood	Scots pine	<i>Pinus sylvestris</i>	Pine ut	
	European beech	<i>Fagus sylvatica</i>	Beech ut	
Heat treated wood	Scots pine (Finland)	<i>Pinus sylvestris</i>	Heat (a)	(Militz 2002)
	Scots pine (France)	<i>Pinus sylvestris</i>	Heat (b)	
	Maritime pine (France)	<i>Pinus pinaster</i>	Heat (c)	
Resin treated Scots pine	Interlace treatment	<i>Pinus sylvestris</i>	Interlace	(Krause <i>et al.</i> 2003)
	Melamine resin treated	<i>Pinus sylvestris</i>	Melamine	(Lukowsky 2002)
Wax	Scots pine	<i>Pinus sylvestris</i>	Wax	
Acetic anhydride	Scots pine	<i>Pinus sylvestris</i>	Acetyl. pine	(Beckers and Militz 1994)
	European beech	<i>Fagus sylvatica</i>	Acetyl. beech	

The prepared samples were coated with several stains (Table 2) according to instructions of the coating manufacture.

One sample per combination of coating and material was exposed with artificial weathering. The dry film thickness was measured microscopically.

Table 2: Summary of coating systems used. (* spray coated)

	Thin film		Medium-thick film			Thick film	
	Thin (a)	Thin (b)	Mid (a)	Mid (b)	Mid (c)	Thick (a)	Thick (b)
wet film thickness	2 x dipped	3 x brush coated	1 x 200 μm^*	2 x 100 μm^*	2 x 200 μm^*	2 x 150 μm^*	2 x 150 μm^*
dry film thickness	35 – 40 μm	35 – 40 μm	45 μm	60 – 70 μm	60 – 70 μm	120 – 150 μm	130 – 150 μm

The samples were tested in accelerated weathering according to prEN 927-6 with two cycles (750h). Each cycle consisted of weekly sub cycles as described in prEN 927-6. A QUV device was used for the weathering cycles. After 750 h artificial weathering, partial damages were added to one half of the exposed surface. A simulation of hailstorm damage was applied two times in the edges and a cross cut was done in the centre of the weathered surface.

Evaluation of cracks, flaking and discoloration were done via a classification system (Table 3) based on visible observation of samples.

Table 3: Summary of classification system

Classification	1	2	3	4	5
Cracks	No cracks	Small cracks in coating	Small cracks in wood	Easily visible cracks	Heavy cracks
Flaking (a)	No flaking		Light flaking		Heavy flaking
Flaking (b)	No flaking		Light flaking		Heavy flaking
Discoloration of wood	No discoloration		Light darkening		Heavy discoloration

RESULTS AND DISCUSSION

Cracking of coating and cracking of wood below the coating is a very important factor, because it damages the primer resulting in damages such as flaking, water uptake or fungal attack. Classification of cracking (Figure 1) shows that the highest cracking is seen on untreated Scots pine sapwood. The shown mean value is calculated from samples of the same material but containing different coatings, therefore the standard deviation is high. The standard deviation shows the variation of coating, which has a strong influence on the cracking as well.

Severe differences between the modification systems are observed. Heat treated Scots pine from France (heat (b)) showed the highest value and acetylated beech wood (acetyl. beech) achieves the lowest classification (best performance). For modified wood which shows a classification of 2 or lower, it could be assumed that the cracking is significantly reduced.

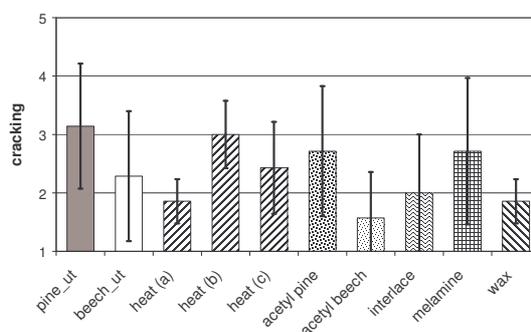


Figure 1: Cracking classification after 1500 h QUV. Mean value of 7 coating variations.

Flaking (Figure 2) was separately evaluated for the areas of samples containing artificial pre-damage (2 treatments to simulate hailstorm and 1 crosscut damage applied after 750 h weathering) and the areas without an artificial damage. The undamaged areas of modified wood except [heat (b)] and [melamine] show lightly improved flaking behaviour compared to untreated Scots pine sapwood. The flaking in the pre-damaged areas yields in a comparable classification for [pine ut], [heat (c)], [melamine], [acetyl pine] and [wax], a light reduced flaking for [acetyl beech] and [interlace] and an increased classification for [heat (a) and [heat (b)].

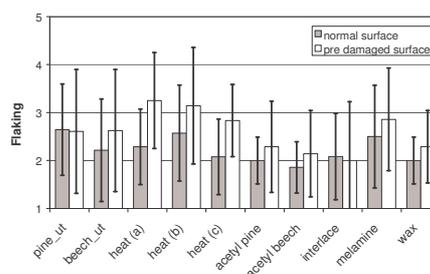


Figure 2: Flaking classification after 1500 h artificial weathering. Classification was separated into the area which was damaged via treatments to simulate hailstorm and crosscut and the undamaged surface. Mean value of 7 coating variations.

The high standard deviation reveals, that the coating itself has a strong influence on the flaking. It can be assumed that the properties of the coating influence the flaking more than the properties of the wood substrate (data not shown). It is known from earlier publications, that some wood modification systems are able to improve the adhesion of a coating, contributing to an improved flaking behaviour (Xie *et al.* 2005).

The discoloration of wood in the undamaged areas provides an impression with regard to the stability of the substrate below the coating (Figure 3). Brownish colour, which is caused by an oxidation of lignin, could be seen on all samples except the heat treated material (which is brownish due to the treatment). Compared to untreated Scots pine, the discoloration is reduced in all modified wood. The heat treated samples show a brightening of the dark brown colour, which can possibly be caused by an oxidative degeneration of chromophores such as phenols (Ayadi *et al.* 2003).

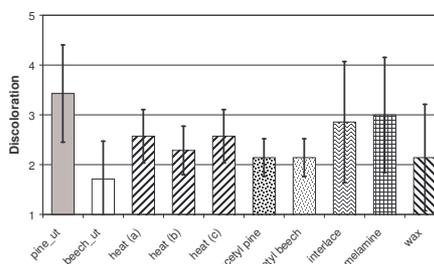


Figure 3: Classification of discoloration of wood surface under the weathered coating. Discoloration is mainly caused by lignin degradation. Mean value of 7 coating variations.

A summary of the mean values of all classified properties demonstrates which combination of modified wood and coating system provides a good performance and which combination seems to be ineffective

(Table 4). For all modified wood, except [heat (a)], [heat (b)] and [wax], at least one coating could be determined which represents a promising combination.

Table 4: Mean value of evaluated properties (rounded to integer).

	Thin film		Middle film			Thick film	
	Thin (a)	Thin (b)	Mid (a)	Mid (b)	Mid (c)	Thick (a)	Thick (b)
pine ut	4	3	2	2	2	3	4
beech ut	3	1	2	1	1	3	3
heat (a)	3	2	2	2	2	2	2
heat (b)	4	2	2	2	3	3	3
heat (c)	3	2	2	2	2	1	2
acetyl pine	3	2	1	2	1	3	3
acetyl beech	2	1	1	2	1	2	2
Interlace	3	1	1	2	1	2	3
Melamine	3	3	2	1	1	4	4
Wax	3	2	2	2	2	2	2

For modified wood [interlace] and [acetyl. beech] 3 different coatings could be determined, resulting in a low classification (good performance) in all investigated properties.

CONCLUSIONS

This investigation was conducted to answer several research aims. Modification of wood results in a reduced cracking and reduced discoloration compared to untreated wood. The observed flaking was more strongly influenced by the used coating system than the wood modification system. The discoloration of the wood surface due to UV light (QUV) could be reduced by the modifications. A further investigation should be done to prove if that the coating properties of modified wood results in an increased durability of coating to reduce maintenance in window frames and enhance the resistance against damage.

Differences between the single wood modifications systems were observed, based on sensitivity against cracks. Reduced swelling and shrinking behaviour together with a low brittleness are the main factors to reduce cracking.

Combinations between modified wood and a coating were found which provide a better weathering resistance than the best combination of untreated Scots pine and the medium-thick film coatings.

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COMPARATIVE INVESTIGATION ON SOME PHYSICAL PROPERTIES OF MODIFIED WOOD

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Keywords: Swelling and shrinking, conductivity, heat capacity, water permeability, Scots pine

ABSTRACT

Scots pine sapwood (*Pinus sylvestris* L.) was treated with modifying agents which display different modes of penetration. Wood modification was performed with two silicone micro-emulsions (SMI I and II), one paraffin product and 1,3-Dimethylol-4,5-dihydroxyethyleneurea (DMDHEU) to study the water permeability, heat capacity and heat transport. In addition, a digital imaging technique was used to obtain swelling and shrinking values. The radial and tangential swelling was diminished considerably (34-37 %) with DMDHEU treatment. The SMI I emulsion (molecule size < 2nm) exhibited stabilisation of wood in the order of 14-19 % compared to SMI II with only 4-10 %. The wax treatment was shown to cause radial stabilisation, but a decrease in the tangential direction. After wax impregnation of pine wood, the heat transport was found to increase, due to a reduction in heat capacity. However, thermal properties of SMI and DMDHEU treated pine remained unchanged and ranged in the same area like untreated pine. The capillary water flow was reduced by half with DMDHEU and by two-thirds in case of SMI. The wax modified material became impermeable for water.

INTRODUCTION

Properties such as thermal conductivity and heat capacity are essential parameters during timber drying and heat processing of wood (Olek *et al.* 2003). Due to its relatively low heat conductivity and heat capacity, wood contributes to the insulation of housing constructions (*e.g.* claddings, walls). Thermal properties of wood are influenced by density, moisture content, anisotropy and temperature (Simpson and TenWolde 1999, Olek *et al.* 2003). Modification of wood (*e.g.* by heat treatment, acetylation) imparts changes in wood, especially in the cell wall. Chemical modifying agents can be deposited in the cell wall (reaction with OH groups), in the lumen of cells, or partly in the cell wall and the lumen, depending on the type of modification. Three types of modification representing different localisation of chemical deposition and pore sizes in wood were studied, since deposition of chemicals in the wood can particularly change properties such as density and hygroscopicity. The different modifications distinguished in the current study were: Agglomeration of modifying agents in the cell lumen (1), deposition in the cell wall (2), deposition in the cell wall and the lumen (3).

The first type of deposition (1) is represented by the wax treatment of wood that is supposed to fill and close rays and cell lumen of tracheids.

Studies on the small molecule sized cross linking DMDHEU suggested that the compound is most abundant in the cell wall (2). SMI is supposed to be deposited in the cell wall as well as in the lumen (3). This paper aims to determine physical properties of modified wood that are of interest when applied in the building industry as construction and isolation material.

EXPERIMENTAL

Wood samples were prepared from Scots pine (*Pinus sylvestris* L.) sapwood with dimensions 35 x 35 x 10 mm³ r x t x l (thermal properties), 20 x 20 x 10 mm³ r x t x l (dimensional stability), 30 x 30 x 20 mm³ (water permeability) and vacuum-pressure impregnated (Table 1) with silicone micro emulsions with 15 % treatment concentration ASE 8160 and SQE 2020 (CHT R. Beitlich GmbH, Germany). A paraffin (Fischer-Tropsch), free of alkenes, aromatics, functional hydrocarbons and sulphur compounds, melting point 80-88°C, was used with 100 % concentration. 1,3- Dimethylol-4,5-dihydroxyethyleneurea (DMDHEU) was used with 30 % concentration in combination with catalyst MgCl₂.6H₂O.

Table 1: Treatment parameters of modified wood.

Treatment	Process	Time	Temperature	Note
SMI I	Vacuum-pressure 100mbar, 12 bar	1h / 2h	20 °C	Heat curing in drying kiln, 40-103°C in raising steps, 14 days
SMI II	Vacuum-pressure 100mbar, 12 bar	1h / 2h	20 °C	Heat curing, 40-103°C in two weeks
Paraffin	Pressure 12 bar	1h	120 °C	Conditioning in climate chamber for 24h
DMDHEU	Vacuum-pressure 100mbar, 10 bar	0,5h / 2h	20 °C	Heat curing (120°C) in drying kiln, 24h

Thermal properties

Heat conductivity k [W·m⁻¹·K⁻¹] and heat capacity c [kJ·kg⁻¹·K⁻¹] of wood were analysed with the microprocessor controlled portable device ISOMET Model 104 (Applied Precision Bratislava, Slovakia).

Dimensional stability

A defined area of modified wood was moistened, and changes during swelling and shrinking in each dimension (radial, tangential and longitudinal) were recorded with a microscope connected to a digital imaging system. Values for swelling and shrinking of modified specimens were related to the control displaying the amount (%) of stabilization after modification.

Water permeability

The non-steady state method was used to determine the permeability. The device based on the atmospheric pressure on the water surface employed to generate the pressure was designed according to Babiak *et al.* (1995). The water flow was analysed in the longitudinal direction according to the method described by Babiak and Hudec (1998).

RESULTS AND DISCUSSION

The thermal conductivity was found unchanged for both silicon emulsions and DMDHEU treated Scots pine. The conductivity of structural lumber at 12 % moisture content is usually in the range of $k = 0.1- 1.4$ W/ (m·K) (Simpson and TenWolde 1999). Požgaj *et al.* (1993) reported $k_l = 0.285$ W/ (m·K) for Scots pine sapwood. Untreated Scots

pine exhibited an average heat capacity of 2.3 kJ/kg·K compared to 2.8 kJ/kg·K when modified with 30 % DMDHEU. The heat capacity was reduced by up to 35 % for the wax treated wood specimens, whereas silicone modification showed no influence on heat capacity regardless of molecule size. The deposition of wax in the cell lumen after impregnation of wood increased the thermal conductivity ($k= 0.34 \text{ W}\cdot\text{m}^{-1}\cdot\text{K}^{-1}$) and decreased heat capacity as a function thereof. DMDHEU ($k= 0.23 \text{ W}\cdot\text{m}^{-1}\cdot\text{K}^{-1}$) and both silicone modifications showed heat conductivity values comparable with untreated wood.

The DMDHEU treatment reduced tangential and radial swelling of Scots pine by more than 35 %. Wax infiltrated wood showed no influence to the dimensional stability. SMI I showed up to 20 % less swelling and shrinking compared to 10 % observed for SMI II. The swelling and shrinking values recorded with digital imaging systems are comparable to data published for silicone and DMDHEU treated wood which were measured diametrically (Krause, 2003).

The obtained permeability coefficients (**k**) were as follows: DMDHEU = 1.55×10^{-13} , SMI I = 5.01×10^{-14} , SMI = 15.01×10^{-14} , SMI II = 4.81×10^{-14} , Scots pine sapwood untreated = 6.5×10^{-14} , Scots pine untreated and extracted with ethanol/cyclohexane = 6.5×10^{-14} . Wax treated specimens were impermeable for water, whereas wood treatment with 30 % DMDHEU obviously resulted in a reduced vessel and pore size available for water penetration. Specimens treated with 15 % concentration of high and low molecular weight silicones were shown to have unchanged water permeability. This is not surprising; they are well known to be water vapour permeable besides their hydrophobicity (Hager 1994).

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RESISTANCE OF MODIFIED WOOD TO MARINE BORERS: RESULTS FROM A FIVE YEAR FIELD TEST ACCORDING TO EN 275

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Keywords: Modified wood, marine borer, *Teredo*, *Limnoria*, durability, field test

ABSTRACT

The resistance to marine borer attack of wood modified by several methods was tested in a field test according to the European Standard EN 275. The wood modification methods were: 1) Furfurylation, 2) Treatment with methylated melamine resin (MMF), 3) Acetylation, 4) Acetylation followed by furfurylation, 5) Acetylation followed by treatment with MMF resin, 6) Maleoylation (using water solution of MG or organic solvent solution of maleic anhydride), 7) Succinylation (with or without post-treatment with copper sulphate solution), 8) Modification with reactive linseed oil derivative (UZA), 9) Treatment with modified rape seed oil, 10) Thermal modification in nitrogen gas (Le bois retifié), 11) Thermal modification in fresh rape seed oil and 12) Thermal modification in old rape seed oil. Wood species used for all treatments was Scots pine (*Pinus sylvestris* L.). Some of the methods used (1, 6-8) were part of an European research project (the *Chemowood* project, FAIR-CT97-3187) and therefore modifications 6-8 was performed by the project participant responsible for the method. Acetylation, furfurylation, MMF-treatment and oil heat treatment were performed by the authors at Chalmers University of Technology or at BFH in Hamburg. The test specimens were put on the test rigs in the bay outside Kristinebergs Marine Research Station in Sweden 150 km north of Gothenburg. The test was started in 1999. The marine borer (mainly *Teredo navalis*) activity at the test site is very high, always resulting in failure of control specimens within a year. Many of the modification methods also result in modified wood with poor resistance to marine borers, in some cases the modified woods seemed even more severely attacked than the controls. However, other methods (furfurylation, MMF-treatment and acetylation followed by MMF-treatment) seem to provide excellent resistance to borer attack.

INTRODUCTION

Very few field tests have been made on resistance of modified wood to marine borers (Tarkow *et al.* 1950, Johnson and Rowell 1988, Larsson 1998). Larsson tested acetylated Scots pine that failed in 2 years. Tarkow *et al.* tested acetylated birch wood with similar results. The study by Johnson and Rowell included Southern pine modified by several different modification methods in the same test. The latter study found the service life of acetylated wood to be 8 years. However, in none of the studies mentioned as many wood modification methods as in the present study were included.

EXPERIMENTAL

Wood materials

The wood material used in the field tests was sapwood of Scots pine (*Pinus sylvestris* L.). All modification methods were applied on pine sapwood. All wood samples came from Hallsjö Brädgård near Uppsala, which delivers samples to most NWPC field tests. The density of the Swedish pine sapwood was approx. 480 kg/m³ and all pine specimens were pure sapwood and free from defects.

Modification of wood

Acetylation and furfurylation were performed in pilot plants at Chalmers University of Technology, whereas modification with methylated melamine resin (MMF resin) and oil heat treatment in pilot plants at BFH. The remaining chemical modifications (maleoylation, succinylation, and modification with reactive linseed oil derivative) were performed by other partners of the CHEMOWOOD project (FAIR-CT97-3187), i.e. VTT (Finland), BioComposites Centre (UK) and SHR (Netherlands). Pine that had been heat treated by the NOW[®] process in a pilot plant at St Etienne (France) was also included in the field test. More information about the modification procedures is described in Epmeier *et al.* (2003).

Location of test site and date of installation

The test rigs were placed on the sea bottom in the bay outside Kristineberg Marine Research Station, 100 km north of Gothenburg, Sweden. Test was started in 1999.

Test site characteristics

Temperature and salinity of water

Temperature varies between 18-22°C in the summer and -1.5°C in mid-winter. Salinity varies between 26 g/kg and 34 g/kg. Good oxygen level due to a strong water flow through the "bay".

Borer activity

Gribbles: *Limnoria lignorum* (present but not very active)

Molluscs: (the characteristics listed, are for the actual test site):

Teredo navalis (most common species), up to 7cm length during one growth season

Nototeredo norvegica, up to 15 cm length during one growth season

There is borer activity all around the year. The most occurring borer species, *Teredo navalis*, is active 11 months out of 12. The criterium for failure due to *teredo* attack (tunnels covering more than 50 % of the specimen area as it appears on the X-ray film) is often fulfilled already within 6 months for untreated control specimens. Maximum "service" life of untreated controls is approx. 1.5 years, after which the samples are often broken to pieces by the autumn storms.

Installation conditions

Specimens were hung on nylon-bars ($\varnothing=24$ mm) of two ladder-like rigs placed on the sea-bottom at 6 ± 0.4 m depth at low tide. The test rigs have heavy concrete foundations and each rig was kept upright by a 50 cm-diameter buoy. As a result of the arrangement, the specimens are

located at depths varying from 4 m to 6.5 m below water surface during the exposure period.

Assessment of wood borer attack

The rigs were taken up with a crane-boat and put on the dock. The extent of fouling (overgrowth) and identification of fouling organisms were made before carefully cleaning the test specimens with a blunt knife and a dish-brush, during which possible attack by *Limnoria* was rated visually. The wood samples were immediately put in running surface sea water after cleaning, taken out for X-raying and immediately put back after this was ready. The X-ray films were developed and the *Teredo* attack rated after inspecting the X-ray films on a light-table. The wood samples that had been given the rating: failure, were rejected and the remaining samples were put back on the rigs which were then put back into the sea.

RESULTS AND DISCUSSION

Species identified on/in the test specimens during the test period

All test specimens were completely overgrown with fouling organisms

Fouling growth species

Alcyonium digitatum (Dead men's fingers), *Balanus crenatus* (Rock barnacle), *Ceramium rubrum* (Red algae), *Chorda filum* (Dead man's rope), *Ciona intestinalis* (Sea squirt), *Enteromorpha intestinalis* (Green algae), *Halichondria panicea* (Bread crumb sponge), *Laminara saccharina* (Sugar kelp), *Meditrium senile* (Plumose anemone), *Membranipora membranacea* (Sea mat), *Mytilus edulis* (Blue mussel), *Polysiphonia* sp. (brown slime algae), *Pomatoseros triqueter* (Keel worm), *Semibalanus balanoides* (Northern rock barnacle).

Other species found in the fouling

Asterias rubens (Starfish), *Cancer pagurus* (Common crab), *Carcinus maenas* (Shore crab), *Hediste diversicolor* (Ragworm), *Idotea baltica* (Baltic isopod), *Psammechinus miliaris* (Green sea-urchin).

Dominating fouling species

Ciona intestinalis, *Mytilus edulis*, *Polysiphonia* sp. and *Pomatoseros triqueter*.

Wood boring species found

Teredo navalis (shipworm), *Nototeredo norwegica* (shipworm, however less frequent occurring), *Limnoria lignorum* (gribble, however less frequent occurring).

Wood borer attack

The extent of gribble (*Limnoria navalis*) attack was limited to a rating of 1 (slight attack) on some of the control samples. None of the modified wood specimens were attacked by *Limnoria*. However, the attack by shipworms (*Teredo navalis* and *Nototeredo norwegica*) on control samples was extensive, always leading to failure in one year (during the test period). See bottom row of Table 1 and Figures 1 and 2.

The UZA modified samples and one set of heat treated samples (NOW-process) were also rejected after only one year due to heavy teredo attack. Wood thermally treated in fresh rape seed oil also failed early

with an average service life of 1.4 years. However, wood thermally treated in modified rape seed oil is only slightly attacked after five years in test. Maleoylated wood and succinylated wood samples, with or without post treatment with copper sulphate, have also failed although the service life was slightly longer. MMF resin treated wood at the lowest retention level of MMF has also failed (1.4 years service life). The reference CCA treated wood samples at the lower retention level failed with a service life of 3.4 years, and the one of the samples at high retention level has also been attacked. This level of CCA treatment usually gives a service life of approx 30 years.

Table 1: Condition of pine sapwood samples (25 x 75 x 200 mm) after 5 years of exposure on test rigs in the bay outside Kristineberg Marine Research Station.

Wood treatment chemical	Chemical retention		No. of samples	No. of samples classified as			Rating, Teroid attack (0-4)	Overall rating	Aver. Service life (years)
	WPG	(kg/m ³)		sound	attacked	rejected			
Furfuryl alcohol (Falc)	11		5	-	-	6	4.0	Failed	4.0
	29		5	-	-	-	0.0	Sound	-
	50		5	5	-	-	0.0	Sound	-
Succinic anhydr. (SA)	13		1	-	-	1	4	Failed	2
	24		1	-	-	1	4	Failed	5
	17-32	5 (Cu)	3	-	1	2	3.7	Failed	-
Maleic anhydride or MG	17-44		4	-	1	3	3.8	Failed	-
Acetic anhydride (Ac)	22% AC		5	3	2	-	0.6	Slight	-
Ac + MMF	21+ 8		5	5	-	-	0.0	Sound	-
	21+19		5	5	-	-	0.0	Sound	-
Ac + Falc	19+ 7		3	1	2	-	0.7	Slight	-
	19+18		3	2	1	-	0.7	Slight	-
MMF resin	11		4	-	4	4	4.0	Failed	4.8
	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	1	4	-	1.0	Slight	-
CCA (NWPC ^a Standard No.1)		4 ^b	6	-	-	6	4.0	Failed	3.2
		18 ^b	6	5	1	-	0.2	Sound	-
Untreated pine sap controls	-	-	8+5 +5+ 5+7	-	-	8+5+ 5++5 +7	4.0 ^c	Failed ^c	1.0 ^c

^aNordic Wood Preservation Council, ^bCuO (19 wt-%); CrO₃ (36 wt-%); As₂O₅ (45 wt-%); ^cThree sets, each lasted 1 year

Acetylated samples (with or without furfurylation post treatment) are only slightly attacked after 5 years which is better than the performance reported by Larsson (1998), but in line the results of Johnson and Rowell (1988).

However, acetylated samples post-treated with MMF-resin (see Figure 3), one set 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 5 years of test.



Figure 1: Control sample (failed due to Teredo attack) that broke when being removed from the rig.

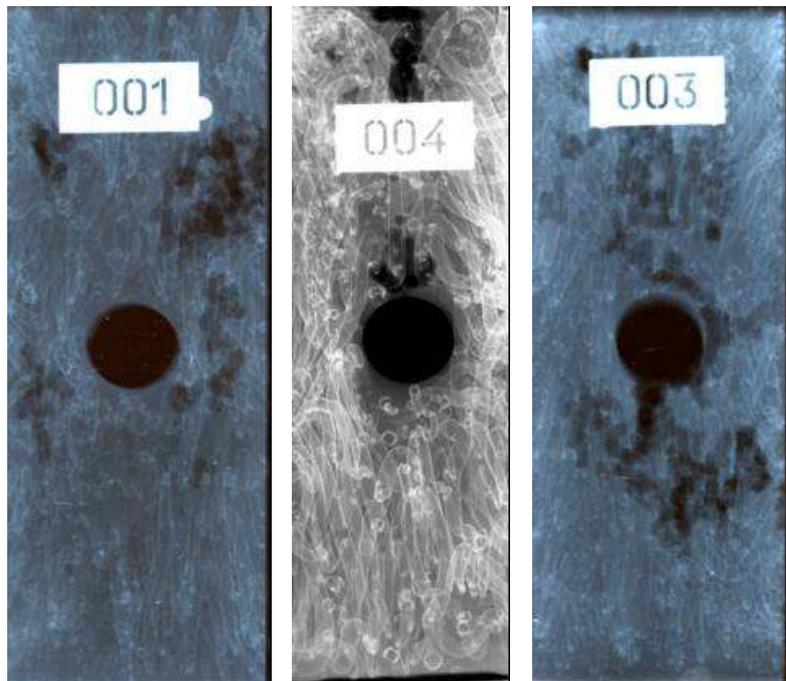


Figure 2: Examples of X rays of failed controls after 1 year (from different years).



Figure 3: Oil Heat Treated (sound) and Acety+MMF, 21+8 (sound) after 5 years.

CONCLUSIONS

- Many types of modified wood have poor resistance to marine borers. Examples of these are: Thermally treated, maleoylated and succinylated wood.
- In one case, wood modified by reactive linseed oil derivative (UZA), the modified woods actually seemed more severely attacked than the controls.
- Other methods (furfurylation, MMF-treatment and acetylation followed by MMF-treatment) seem to provide excellent resistance to borer attack.

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CHEMICAL MODIFICATION OF WOOD WITH CITRIC ACID

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Keywords: Wood, chemical modification, dimensional stability, non-formaldehyde agents, citric acid, DMDHEU

ABSTRACT

A new non-formaldehyde crosslinking system has been developed, composed of citric acid (CA) and a phosphino-based catalyst, offering beneficial environmental advantages. For the purpose of chemical modification for the improvement of the dimensional stability, fir wood (*Abies alba* Mill) and beech wood (*Fagus sylvatica* L.) were impregnated under vacuum. Effects of the treatment were compared with 1,3-dimethylol 4,5-dihydroxy ethylene urea (DMDHEU) treatment. The esterification reaction between CA and cellulose was evaluated by Fourier Transform Infrared (FTIR) spectra. Dimensional stability of modified wood was determined by anti-shrink efficiency (ASE) using the water soak / oven dry method. The results showed an improvement of ASE in the case of both agents, but higher with CA. Among other benefits, the formation of network structures between wood and reagent components have improved the mechanical properties, expressed as microtensile strength.

INTRODUCTION

Since wood consist of approximately 50 % of cellulose there are many similarities with cotton textiles, which mainly consists of cellulose - up to 98 %. For that reason the agents that have showed good results in textile finishing applications can be applied for chemical modification of wood as well. Such reagents used until now are all based on N-methylol (represented by DMDHEU). These agents form ether linkages accelerated with a Lewis acid catalyst (MgCl₂). The greatest problem associated with their usage is formaldehyde release, which occurs under elevated temperatures. Formaldehyde is toxic, potentially carcinogenic and might cause dermatitis in direct skin contact (Soljacic 1988, Katovic 1988). This has led to interest in the development of non-formaldehyde agents (Bischof Vukusic 1999) and catalysts (Welch 1994, Bischof Vukusic 2002). For the purposes of wood modification, CA and SHP catalyst were applied in this study and the results obtained with this new class of non-formaldehyde agents are compared with DMDHEU agent, which has already been applied for wooden substrates (Militz 1993, Xie 2005).

EXPERIMENTAL

Material / Method

The samples for dimensional stability measurements were 20 × 20 × 10 mm (T × R × L). After conditioning at 20°C and 65 % relative humidity, the samples were impregnated under vacuum, with citric acid (CA) or DMDHEU solution. Control samples were impregnated with distilled water. The impregnation was performed under a vacuum of

2 kPa for 3 hours and followed by 18-hours soaking at atmospheric pressure. Some of the control samples were impregnated with distilled water and air-dried (Control 1) while the others were heated at 140 °C for 10 hours (Control 2).

Table 1: Sample treatments

Samples	Agent	Catalyst	Thermal treatment
Control 1	Water	/	20 °C
Control 2	Water	/	140 °C
Impregnation 1	7 % CA	6.5 % SHP	140 °C t = 10 h
Impregnation 2	12 % DMDHEU	1.8 % MgCl ₂	140 °C t = 10 h

Dimensional stabilisation

Dimensional stabilisation was quantified by comparing the volumetric swelling coefficients of treated and control samples. After treatment and air drying, all samples were oven dried at 70 °C to constant weight and then vacuum impregnated with distilled water and soaked for 24 hours. The volumetric swelling coefficient (S), reduction in water absorption (R), and antismelling efficiency (ASE) were calculated using the equations:

$$\alpha_v (\%) = 100 (V_s - V_o) / V_o; R (\%) = 100 (w_c - w_t) / w_c; ASE (\%) = 100 (\alpha_{v,c} - \alpha_{v,t}) / \alpha_{v,c}$$

where are: *V*– volume, *s*– saturated, *o*– oven dried at 70 °C, *w*– moisture content, *c*– control, *t*– treated.

Tensile strength

Tensile strength and FTIR measurements were performed on conditioned veneers of precise thickness cut by microtome according to the technique described by Derbyshire *et al.* (1995). Dimensions of each veneer were 60 mm × 10 mm × 100 mm (T × R × L). Measurements were performed on a Pulmac zero-span tensile tester (Pulmac International Inc. USA).

FTIR spectroscopic analysis

Veneers modified with CA or DMDHEU solution at two different concentrations were washed with 0.1 M HCl or with 0.1 M NaOH for 2 minutes before spectroscopy (Choi 1994).

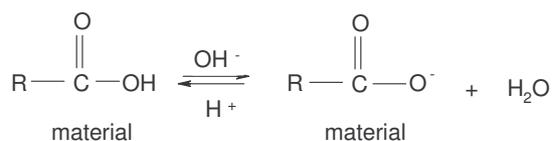


Figure 1: Scheme of carbonyl / carboxyl balance at treated material

Samples were treated with NaOH solution to convert free carboxyl to carboxylate anions (Fig.1), so that the ester carbonyl band can be separated from the overlapping carboxyl carbonyl band. The ester carbonyl band absorbance in the infrared spectra was normalised against the 1318 cm⁻¹ band, associated with the C-H bending mode of cellulose.

RESULTS AND DISCUSSION

Dimensional stability

The results of anti swelling efficiency (ASE), are shown in Table 2, showing that wood treated with CA had an improved ASE of about 40 %, with both wood species. In the case of DMDHEU, the ASE was lower, which emphasises an additional reason for the usage of the ecologically more favourable CA. Results of water absorption reduction showed more noticeable impact of wood species. In the case of fir wood the results of R are similar with both agents, but in the case of beech wood results are more favourable in the case of DMDHEU treatment.

Table 2: Influence of wood species and type of chemical treatment on dimensional stability

Wood species	Agent / Treatment	α_v^1	R ² (%)	ASE ³ (%)	Coeff. var. (%)
FIR (Abies alba Mill.)	Water / 20°C	16.27	/	/	
	Water / 140°C	16.87	/	/	
	CA+SHP	8.57	23.83	43.15	25.75
	DMDHEU + MgCl ₂	9.60	19.96	38.55	14.31
BEECH (Fagus sylvatica L.)	Water / 20°C	20.08	/	/	
	Water / 140°C	23.45	/	/	
	CA+SHP	13.65	25.68	41.00	15.96
	DMDHEU + MgCl ₂	14.95	6.78	31.09	24.31

¹Volumetric swelling coefficient, ²Reduction of water absorption, ³ASE - anti swelling efficiency

Tensile strength

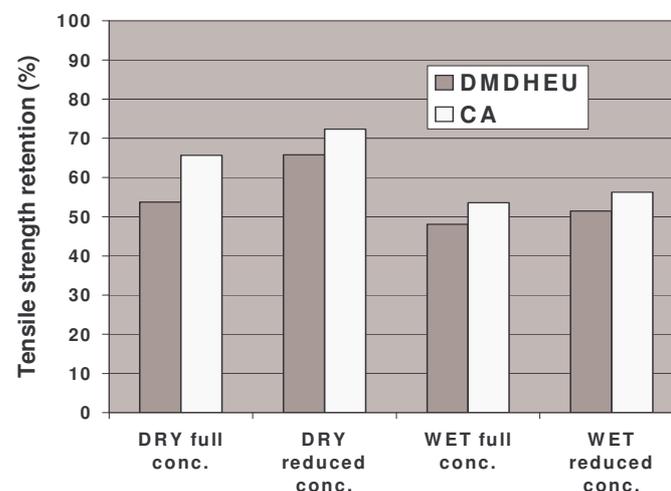
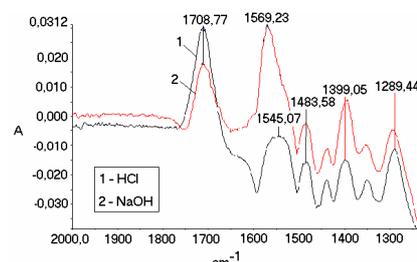
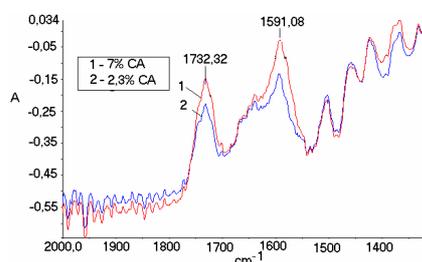


Figure 2: Zero span test - microtensile strength of fir wood in dry and wet state

The main problem associated with DMDHEU treatments is reduction of mechanical properties, primarily tensile strength. A possible cause of this tensile strength loss is the formation of complexes of MgCl₂ with DMDHEU (Yang 2000). Our results have confirmed that hypothesis, since with the usual concentration of 12 % DMDHEU values of tensile strength retention are even lower than 50 % in the case of samples tested in a wet state. Using a lower concentration of agents has caused reduced tensile strength losses, which is particularly noticeable in the

wet state where the results are improved up to 62 % (Fig. 2). Application of citric acid and SHP catalyst have produced more favourable results compared to DMDHEU, since a reduction of tensile strength is lower in all cases. These results are giving additional value for the usage of CA.



FTIR spectroscopic analyses

Figure 3: FT-IR spectra of veneers treated with 7% CA (after treated with HCl and NaOH)

Figure 4: FT-IR spectra of veneers 7% and 2.3% CA

Samples treated with HCl have shown maximum peak intensities at 1730 cm^{-1} , which represents total amount of carbonyl groups in esters formed between CA and cellulose plus carbonyl groups in unesterified free carboxylic groups of CA. As shown in Figure 3, peaks of acid-rinsed samples at 1730 cm^{-1} have reached maximum values, while they are significantly lower measured on alkali-rinsed samples. Treatment of samples in alkali solution converted unesterified free carboxylic groups to carboxylates with peaks at 1585 cm^{-1} . Infrared spectra of samples treated with two concentrations of CA solutions in the presence of NaH_2PO_2 catalysts are presented in Figure 4. FT-IR analyses have confirmed that a higher concentration of agent forms a larger amount of ester on the wood.

CONCLUSIONS

These results clearly demonstrate that the dimensional stability of wood can be substantially improved using this new class of ecologically acceptable agents, which are cheap and easily available. Strong covalent bonds have been formed between the reactant - CA and cellulose hydroxyls. A high number of these crosslinks, confirmed by FT-IR analyses, yields good values of antismellinng efficiency (approximately 40 %). Application of citric acid has produced more favourable results of tensile strength retention compared to DMDHEU. Infrared spectroscopic data demonstrated that the ester crosslinking of citric acid treated veneers can be examined on a semi-quantitative basis by measuring the ester carbonyl band intensity and the carbonyl band intensity ratio (ester/carboxylate).

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DURABILITY PROPERTIES OF RUBBER AND PAULOWNIA WOOD TREATED BY HYDROPHOBATION AGENTS

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Keywords: Water repellent, durability, blue stain, mechanical properties, *P. fortunei*, *H. Brasiliensis*

ABSTRACT

Rubber (*Hevea brasiliensis*) and paulownia (*Paulownia fortunei*) wood were treated with three different water repellent dispersions based on paraffin, a modified N-methylol compound and silicone. Water uptake was reduced by all treatments. All treatments enhanced the durability related to basidiomycete and soft rot decay. Blue stain effectively diminished, particularly after treatment with the modified N-methylol compound. Mechanical properties of both wood species tested were not affected, because of a controlled curing.

INTRODUCTION

Rubber wood (*Hevea brasiliensis*) is one of the most popular timbers for making furniture and other wood based products in Asia (Balsiger *et al.* 2000). Paulownia (*Paulownia fortunei*) is an extremely fast growing tree with an average growth of two meters per year in height and 4-5 cm in diameter and of very low density (Chinese Academy of Forestry Staff 1986). Cultivation of these species in plantations could help to reduce depletion of forest resource from natural stands, timber shortages and ecological imbalance in many Asian developing countries. Upgrading of these species through chemical modification could enhance their material properties and competitiveness compared to more durable species and species from natural stands. In this study, *Hevea brasiliensis* and *Paulownia fortunei* wood were modified with hydrophobation agents based on paraffin, a modified N-methylol compound and silicone.

EXPERIMENTAL METHODS

Wood samples were cut from 30 year-old *Hevea brasiliensis* and 8 year-old *Paulownia fortunei* from Vietnam. The chemicals used were a formulation of a modified N-methylol compound (FNM) combined with a catalyst, a paraffin emulsion (AP) and a silicone emulsion (ES). Wood specimens were impregnated using 1 h vacuum at 50 mbar and subsequently 2 h pressure at 12 bar. The concentration of the treatment solution was 30% related to the stock solution. The number of replicates is given in Table 2. Control samples were treated with water. *Conventional curing* (I) was performed directly in an oven for specimens of small size. *Steam-bag curing* (II) was done in a pierced heat resistant plastic bag (Table 1). The assignment of the sample size and the curing method to the experiment is shown in Table 2. The uptake of chemical after curing was expressed as weight percent gain (WPG).

Table 1: Curing condition for treated samples

Curing		Increasing temperature				
Convention, 85h	I	40°C-48h	60°C-4h	90°C-14h	103°C-3h	120°C-16h
Steam-bag, 56h	II	40°C-15h	60°C-10h	90°C-15h	103°C-10h	120°C-6h
	III	40°C-15h	60°C-10h	90°C-15h	103°C-10h	120°C-16h

Table 2: Curing method and sample size related to the experiments

Experiment and replicates	Size, mm	Section	Curing
Water uptake & EMC, 10	25 x 25 x 10	rad x tan x long	I
Blue stain, 12	5 x 40 x 40	mixed rad+tan x long	I
Basidiomycetes (4), 9	5 x 10 x 30	mixed rad+tan x long	I
Soft-rot (arc. ENV 807), 10	5 x 10 x 100	rad x tan x long	I
Modulus of elasticity and rupture, 10	20 x 20 x 360	rad x tan x long h	II
Hardness, 10	42 x 42 x 42	rad x tan x long	III

Water uptake was determined by dipping the samples in water for 120 h; a vacuum (100 mbar) was applied after 96 h. Subsequently, the samples were weighed and the water uptake was related to the dry weight of the samples after treatment. Modulus of elasticity (MoE) and bending strength (MoR) and hardness were measured according to DIN 52186, EN1534 and ISO 3350. For the blue stain experiments *Aureobasidium pullulans* was sterilely grown on malt agar in a Petri dish. Four sterile treated or untreated wood samples were placed on the agar with mycelium at the Petri dish centre by using metal grids as spacers. The samples were additionally inoculated with an infected agar disk (1 cm in diameter). After 8 weeks of incubation, the samples were classified in five groups (Figure 1). Both sides of the wood samples were rated (underside: on agar; top side: with mycelium disk).

- 0: No blue stain on the surface of sample
- 1: A little circle of blue stain closely grown surrounding the position of inocula at the specimen centre
- 2: Less than 25%
- 3: 25 - 75%
- 4: Higher than 75%

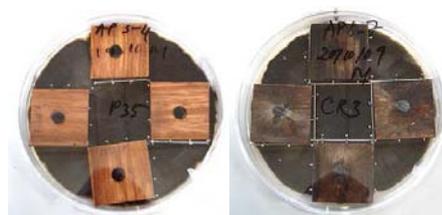


Figure 1: Blue stain classification based on surface infection area (%)

Resistance against the white-rot fungus *Trametes versicolor* and the brown-rot fungus *Coniophora puteana* was determined in a mini-block test (Bravery AF 1978) over 8 weeks following EN 113. Resistance against soft-rot was determined over 5 months according to ENV 807. The loss of modulus of elasticity (MoE) was used to determine the decay rate.

RESULTS AND DISCUSSION

Water uptake

Untreated *P. fortunei* (250 %) showed a much higher water uptake when fully saturated than *H. brasiliensis* (100 %). This can be explained by the porous structure of *P. fortunei* with a high number of vessels and large diameter of lumen (Mai *et al.* 2002). These differences in density resulted in a much higher WPG of treated *P. fortunei* than in case of *H. brasiliensis*. All of the results showed low water uptake of wood treated by FNM, ES and AP (Figure 2).

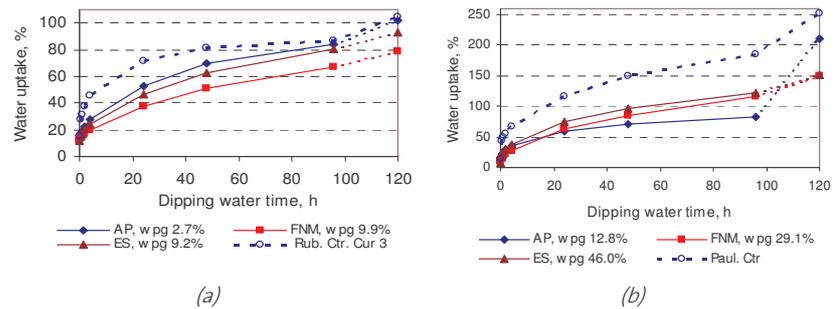


Figure 2: Water uptake of samples treated with 30% solution of FNM, ES and AP (a: *H. brasiliensis*; b: *P. fortunei*)

Blue stain

Untreated *P. fortunei* showed a higher natural resistance against infection by *A. pullulans* (top: 2.9) than *H. brasiliensis* (top: 4.0), probably because of the high extractive content (8.2 %) in *P. fortunei* wood (Mai *et al.* 2002). All treatments significantly reduced staining (Table 3). The infection was always lower in *P. fortunei* samples when compared to *H. brasiliensis* which was equally treated. The highest protection was gained with FNM, followed by ES and AP. Higher effectiveness of ES than AP might be explained with higher WPG of AS.

Table 3. Rating of blue stain (*A. pullulans*) infection of *H. brasiliensis* and *P. fortunei* wood

Treated wood	top side	bottom side		<i>H. brasiliensis</i>	<i>P. fortunei</i>
Hevea brasiliensis			Ctr.		
AP, wpg 6.0 %	3.9	4.0			
FNM, wpg 8.4 %	2.0	2.3			
FNM, wpg 11.8 %	0.7	1.5			
ES, wpg 10 %	2.5	3.3	AP, wpg 6.0 %		
Rubber. Ctr	4.0	3.9			
Paulownia fortunei			FNM, wpg 11.8 %		
AP, wpg 16.8 %	1.0	0.1			
FNM, wpg 12.2 %	0.9	0.5			
FNM, wpg 24.6 %	0.3	0.3			
ES, wpg 44.2 %	0.2	0.2			
ES, wpg 62 %	0.3	0.3	ES, wpg 62 %		
Paulonia. Ctr	2.9	1.0			

Resistance against basidiomycetes

The weight loss of *H. brasiliensis* and *P. fortunei* treated with AP, FNM and ES was low after 8 weeks attack by *T. versicolor* (Table 4). Treatment of *H. brasiliensis* with AP, FNM and ES significantly reduced the weight loss caused by *T. versicolor*, while that of the control was high (Table 5). However, *C. puteana* caused a very low weight loss (below 8 %) of all *P. fortunei* samples. This can be explained with a very high water uptake of the specimens (250-300 %) from the agar media during the incubation.

Table 4: Weight loss of wood samples caused by *T. versicolor* and *C. puteana*. Control values relate to the group of treated samples in the same petri dish.

	<i>H. brasiliensis</i>				<i>P. fortunei</i>			
	FNM	AP	ES	Control	FNM	AP	ES	Control
<i>T. versicolor</i>	7.0	11.8	7.9	43.9	4.7	6.5	3.7	35.5
<i>C. puteana</i>	4.9	6.6	17.4	35.4	--	--	--	--
WPG [%]	6.1	3.8	8.0		14.6	24.5	45.5	

Soft-rot

Dynamic MoE of untreated wood species decreased by more than 70 % over 20 weeks of incubation. Treatment with AP and ES reduced the MoE loss by almost 50 % to about 40 % after 20 weeks. FNM imparted the strongest resistance to soft-rot with a MOE loss of 13.4 (*H. brasiliensis*) and 11.2 % (*P. fortunei*) after 20 weeks (Figure 5, Figure 6).

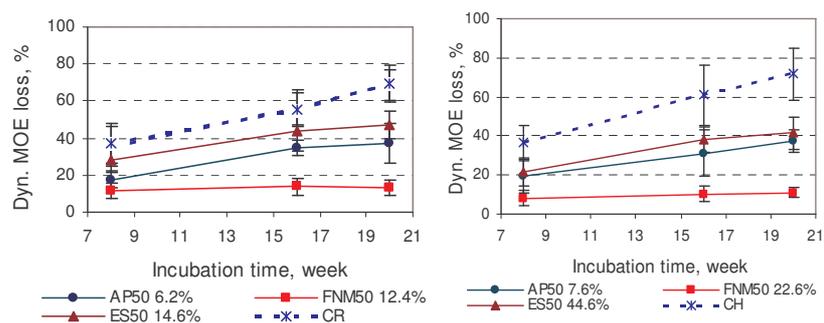


Figure 5: Dynamic MoE loss of treated *H. brasiliensis* (left) and *P. fortunei* wood (right) in soil-bed test - ENV 807

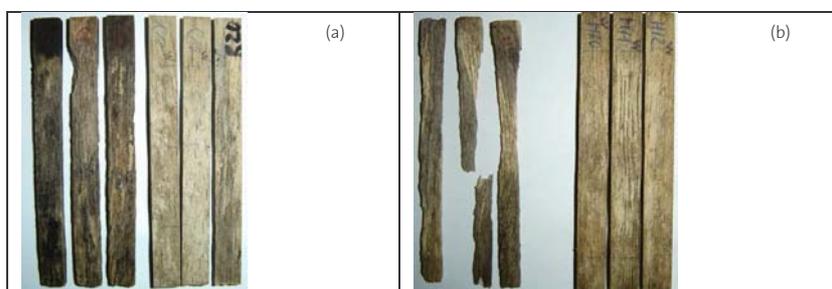


Figure 6: Soft-rot decay of untreated and treated FNM *H. brasiliensis* (a) and *P. fortunei* wood (b) in soil-bed test - ENV 807

Modulus of elasticity and rupture

Treatment with water repellents tested did not reduce the MoE and MoR of *H. brasiliensis* and *P. fortunei* wood. The MoE and MoR of treated *H. brasiliensis* reached a maximum at 11393 N/mm² and

92.8 N/mm² respectively. A maximum MoE and MoR of the treated *P. fortunei* wood can be reached at 5225 N/mm² and 38 N/mm².

Hardness

Janka hardness was not affected due to water repellent treatment. Janka hardness of *H. brasiliensis* and *P. fortunei* wood treated with a modified N-methylol compound and a silicone were in the range of 4500 – 5500 N and of 2000-2500 N respectively.

CONCLUSIONS

Treatment with water repellents imparted hydrophobic properties and enhanced the resistance of wood from *H. brasiliensis* and *P. fortunei* against white, brown and soft rot fungi. Blue stain was significantly reduced through treatment with FNM. This can be partly explained due to the use of the catalyst, which has biocidal properties. Mechanical properties of treated wood were not affected through the treatment. Paraffin-based water repellents (FNM, AP) are low price products and easy to handle on an industrial scale. Thus, treatment with these compounds appears viable in practice.

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SYNTHESIS AND PROPERTIES OF MODIFIED PEG WITH ANTIOXIDATIVE PROPERTIES FOR WOOD DIMENSIONAL STABILISATION

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Keywords: Antioxidant, archaeological wood, PEG, wood dimensional stabilization

ABSTRACT

Archaeological wood recovered from most environments is generally strongly altered due to biotic and abiotic degradation. Such waterlogged wood may be subject to significant deformation upon drying, requiring the use of appropriate conservation techniques to retain the structural integrity. Polyethyleneglycols (PEGs) are the main compounds used to treat such archaeological waterlogged wood. PEGs, like numerous polyethers, are susceptible to oxidation and especially photo-oxidation. Such degradation damages the physical properties of PEG, resulting in scission of the polyether chains, incompatible with successful treatment of waterlogged wood. In this context, we have investigated the synthesis of a PEG bearing a hindered phenol or amine moiety to prevent oxidative degradation. Stability of these products towards photo-oxidation and thermo-oxidation was studied.

INTRODUCTION

Archaeological wood recovered from most environments is generally strongly altered due to biotic and abiotic degradation. Such waterlogged wood may be subject to significant deformation upon drying, requiring the use of appropriate conservation techniques to retain the structural integrity. Polyethyleneglycols (PEGs) are the main compounds commonly used to ensure a long term preservation to such archaeological wood. Soluble in water, low molecular weight PEGs, like PEG 400, are able to diffuse into the wood structure to replace water in cellular walls to increase the wood dimensional stability, while higher molecular weight PEGs (PEG 4000) are able to enhance the wood mechanical resistance by filling the lumens. However, PEGs are sensitive to thermal and photochemical oxidation reactions (Glastrup 1996, Han *et al.* 1996, Morlat and Gardette 2001). In particular, formate end groups are produced, either by heating PEGs at 60-70°C, or under UV irradiation, through a macromolecular chain β -scission leading to a reduction of mechanical properties. Both mechanisms of degradation require the presence of atmospheric oxygen.

Our goal consisted of functionalising PEGs with antioxidant moieties, to protect the polyethers from oxidation, taking advantage of the chain extremity hydroxyl groups to graft different kinds of widely-used compounds in polymer chemistry: hindered phenols like butylated hydroxytoluene (BHT) and hindered amine light stabilisers (HALS). The resistance to oxidation of modified PEGs was then evaluated and compared to free-PEGs and ad-mixed antioxidant-PEGs.

EXPERIMENTAL

Synthesis of grafted PEGs

According to the commercial availability of the required antioxidant moieties, the grafting was carried out by different methods on PEGs provided by Arc-Nucleart or Aldrich. These were either, by direct Fischer esterification between the PEGs and the 3-(3,5-di-*tert*-butyl-4-hydroxyphenyl)-propionic acid, easily obtained by saponification of Irganox 1076 kindly supplied by CIBA (Figure 1). Or, by reaction with 3-(3,5-di-*tert*-butyl-4-hydroxyphenyl)-propionyl chloride which can be performed under much milder conditions (Bergenudd *et al.* 2002).

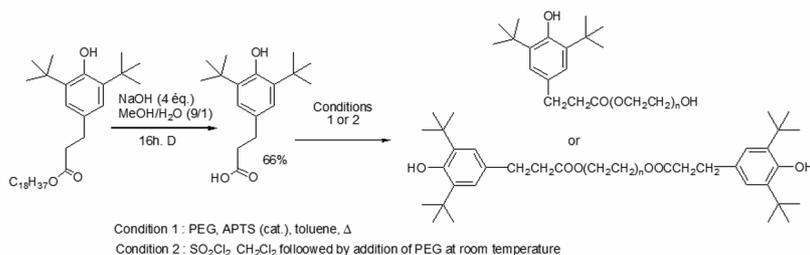


Figure 1: Preparation of PEG modified with hindered phenol moiety

Grafting of the hindered amine moiety was investigated by reaction of the glycidic ether synthesised from epichlorhidrin and N-methylated or 2,2,5,5-tetramethyl-4-piperidinol with PEG in the presence of a catalytic amount of DMAP (Figure 2):

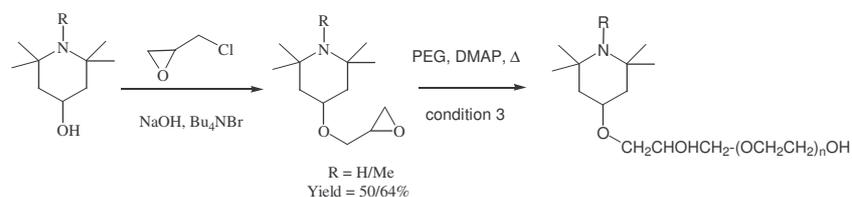


Figure 2: Preparation of PEG modified with hindered amine moiety

Oxidation kinetic studies

Thermo-oxidation experiments were carried out in air at 55°C. To study their stability to photo-oxidation, films of grafted PEGs were irradiated in a SEPAP 12-24 unit at λ ffl 300 nm and 35°C. The formate group generation was monitored by FT-IR, mainly at 1725cm^{-1} , to obtain degradation kinetic curves. Because of the need for solid films, this analysis was only possible on high molecular-weight PEGs (ffl 4000) with a high fusion temperature.

RESULTS AND DISCUSSION

Grafted PEGs synthesis

The results of the PEGs grafting step are given below (Table 1)

Table 1: Results of grafting

PEG	Antioxidant moiety	Conditions	Yield (%)
400	BHT (2 eq.)	1	76
400	BHT (1 eq.)	2	50
4000	BHT (2 eq.)	1	94
4000	BHT (1 eq.)	2	59
4000	BHT (2 eq.)	2	87
10000	BHT (2 eq.)	1	97
400,000	HALS (1 or 2 eq.)	3	100

It was possible and interesting to synthesise the grafted PEGs with one or two antioxidant moieties to get a partial control of the products solubility in water. Yields were generally good.

Antioxidant properties of the grafted PEGs

In thermal conditions, a sample of PEG 4000 with only 0.1 % of hindered phenol grafted PEG exhibited the highest resistance to oxidation, better than that of mixture of PEG 4000 with 0.1 % BHT. Comparatively, decomposition of the PEG 4000 alone started earlier after approximately 900 hours. This high value can be explained by the presence of antioxidants added in the commercial PEG.

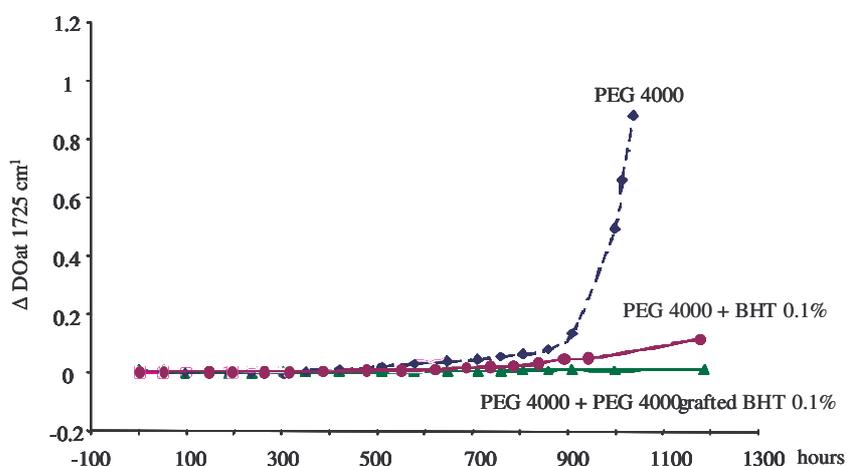


Figure 3: Thermo-oxidation kinetic

In photo-oxidation, the grafted PEGs behaviour observed was completely different, since the degradation of PEGs mixed with hindered phenol grafted PEGs was faster than with the free-PEGs. The oxidation kinetics depended directly on the concentrations of grafted polymer added, indicating a more important photo-inductive effect than the antioxidant effect of the grafted hindered phenol moiety. The photo-oxidation of the hindered amine grafted PEGs were then evaluated, but gave the same kind of results as with the grafted hindered phenol PEGs. An explanation could be the photo-sensitivity of the ether-oxide function linking the HALS moiety to the PEGs.

CONCLUSIONS

Organic polymers are widely used in the restoration of archaeological items and particularly waterlogged wood. Polyethylene glycols (PEGs), water-soluble polyethers, are at present used for consolidation treatment of waterlogged wood, but their sensitivity to oxidation, leads to the loss of polymer consolidation properties. In order to improve the treatment duration, PEGs were stabilised by antioxidant grafting. The evolution of the grafted PEG samples degradation was followed by spectroscopic methods and compared to unstabilised PEG samples. The efficiency of a phenolic antioxidant was shown in thermo-oxidation experiments. However, the light sensitivity of BHT creates an inductive effect on the polymer photo-oxidation, which leads to competition with its stabiliser effect. A solution could be the addition of UV absorbers to the formulation.

The experimental results obtained with the HALS antioxidants show that grafting with an ether function is inefficient in preventing photo-oxidation. The synthesis of a HALS grafted PEG with ester functionality is in progress.

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FIELD PERFORMANCE OF COATED MODIFIED WOOD PANELS

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Keywords: Modified wood, coating, EN 927, above ground, field test

ABSTRACT

The performance of modified wood panels with different types of wood coatings was tested in a field test according to the European Standard EN 927-3. The modified pine substrates were: heat treated (ThermoWood™ D+), low-furfurylated (VisorWood™), and acetylated Scots pine. Heat treated spruce (Spruce ThermoWood D+) was also included and the reference wood substrates were: pine sapwood treated with a copper-organic and metal-free preservatives, Scots pine heartwood, Siberian larch heartwood and European oak heartwood.

The five coating types were: a solvent-borne (SB) white alkyd paint, a white system paint (SB alkyd primer + WB acrylic top), a SB red semi-transparent alkyd paint (ICP), a WB brown semi-transparent acrylic paint and a non-stained SB Tung tree oil.

The coated panels, with and without a water trap according to Annex F in EN 927-3, were exposed on racks, at 45° angle to the horizontal, facing south, and assessed after one year in field. The panels were assessed in respect to surface disfigurement by mould growth or dirt, colour change, cracking, blistering, flaking and paint adhesion strength.

After one year exposure the tung oil film was gone on all panels. However, the oiled modified wood substrates were less covered by mould growth than the control and reference treated panels. Especially the furfurylated pine substrates were performing well with insignificant mould growth.

Thermowood performed well with all other coatings whereas furfurylated and acetylated performed better with the acrylic coating than the alkyd coatings.

INTRODUCTION

Acetylation, furfurylation and thermal modification are three, relatively new processes developed for enhancement of wood. The properties of these materials are well described in the literature (Larson 1998, Sailer *et al.* 2000, Bengtsson & Jermer 2002, Kamdem *et al.* 2002, Epmeier *et al.* 2004, Lande *et al.* 2004). In above ground applications, such as facades, decking, windows etc, with long maintenance intervals, high durability and an acceptable appearance, the use of a suitable surface treatment is in most cases a requirement.

Few studies have been carried out with the objective to evaluate the interaction between modified wooden material and different surface coating systems. A study in progress performed by Norwegian institute

of Wood Technology (Jacobsen 2002, Jacobsen & Evans 2003) has its main focus on generating cladding and decking with a minimum maintenance level of 10 years. Different wood qualities, metal free preservatives, pressure treatments and a few modification methods are tested with different surface treatment systems. Field tests (modified EN 927-3 and other above ground field tests) and Mycologg (Gobakken 2004), an accelerated mycological laboratory test, have been used as test methods. The final results are not published, but the overall impression after 4 years of testing is that the topcoat is the deciding element when evaluating disfiguring fungi and gloss (Jacobsen pers.com 2005). Degree of colour change, cracking and flaking seems to be more due to the interaction between the treated / untreated wood and the chosen coating system.



Figure 1: 13 year old field test of acetylated (the 4 panels in the middle) and unmodified wood panels (the 2 panels to the right) coated with alkyd primer followed by acrylic top coating.

The improved field performance of coated wood panels by use of modified wood substrate was clearly illustrated by the earlier results (Larson 1998, Ekstedt 2002) with acrylic coating on acetylated wood (Figure 1). The coated acetylated wood panels were in astonishingly good condition after 13 years in field, whereas the coated control panels would have needed repainting already after 5 years. In the same trial an alkyd coating system (alkyd primer + alkyd top) performed slightly poorer than the alkyd on the control panels, indicating that the more acidic surface of the acetylated panels increased the aging of the alkyd coating (making it more brittle), and that an alkyd coating system is unsuitable for acetylated wood whereas an acrylic coating is very suitable.

Finnish studies have shown that weather resistance of heat-treated wood was improved by both water- or solvent-borne paints (Jämsä 1999, Jämsä *et al.* 2000) due to better dimensional stability of the wood. By the means of the process described by Jämsä *et al.* 2000 no change in coating recommendations are needed when considering coating of heat-treated wood.

It is well known that colonization of disfiguring fungi on wood might make the wood more susceptible to attack by decay fungi (Bjormann 1988). It is also recognized that some disfiguring fungi can penetrate the paint film and thereby colonize on the wood beneath the paint film (Winters *et al.* 1978, Bravery & Miller 1980, Sharp & Dickinson 1992, Bardage 1997). Most of the experimental studies regarding disfiguring fungi on coated wood have been done with *Aureobasidium pullulans*. Other fungal species, such as *Hormonema* sp., *Cladosporium* sp. and *Phoma* sp., are also recognized as common disfiguring fungi on painted and unpainted wood (Bjormann 1988, Nussbaum 2002). Less is known about their ability of penetrating the paint film. It is of importance to isolate and identify the fungal species causing the disfiguration according to type of wood material and surface coating system. This will bring in valuable knowledge on specific disfiguring fungal species and their preferable surface materials, and thereby be an element when designing sustainable coating systems and wood material.

The aim of this study was to evaluate the field performance of wood panels undergoing 3 different modification (acetylation, furfurylation, thermal modification) in combination with 5 different surface coating systems. Surface disfigurement by mould growth or dirt, colour change, cracking, blistering, flaking and paint adhesion strength were evaluated after one year in order to find sustainable combination for above

ground applications. Additional assessments of fungal disfigurement were done after two years to identify the specific fungal species.

EXPERIMENTAL

Wood materials

The main wood material used in the field tests was Scots pine (*Pinus sylvestris* L.). All modification methods and reference preservative treatments were performed on Scots pine sapwood. The Scots pine for all treatments came from Hallsjö brädgård outside Uppsala, Sweden, except pine for heat treatment that came from Derome sawmill near Gothenburg, Sweden. The Norway spruce (*Picea abies* L.) for heat treatment also came from Derome sawmill. The Scots pine heartwood came from a PhD project at Växjö University, Sweden. The Siberian larch (*Larix siberica* L.) heartwood came from a Swedish window manufacturer and the oak (*Quercus robur*) heartwood came from a sawmill in southern Sweden.

Wood modification

Acetylation was performed in A-Cell's pilot plant at Chalmers University of Technology, Gothenburg, Sweden. Furfurylation was performed at the R&D centre of Wood Polymer Technology ASA in Moss, Norway (now moved to Porsgrunn, Norway). The thermal modification was done by Stora-Enso in the *Thermowood*[®] production plant in Honkalahti in Finland.

Acetylation

The acetylation was carried out according to Rowell *et al.* (1985), in a pilot plant with a microwave-heated 800 litre reactor. Before being treated, the wood specimens were vacuum-dried to a moisture content of about 4%. 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). Unfortunately, the vacuum-drying process prior to the acetylation, was run too fast, resulting in slightly burned heartwood with lots of cracks. However, these problems were not discovered until after the acetylation process and the panels were produced by splitting the acetylated boards (both acetylated and the few left-over non-acetylated boards were slightly burned and cracked in the middle).

Furfurylation

The furfurylation was carried out according to the 2003 year production process at the R&D centre of Wood Polymer Technology ASA in Moss, Norway. Pine sapwood panels were impregnated with a 22% solution of furfuryl alcohol in water (30 parts FA in 100 parts water + acidic catalysts and process additives). The impregnated panels were transferred to a curing oven, where the curing was started with periods of steaming at 100°C. After a curing period of 4h the panels were dried/post cured in a conventional kiln.

When the furfurylated panels were delivered to SP, most of the panels had drying cracks, indicating that the drying schedule used was too short.

Thermal modification

The thermally modified wood panels were taken from 4m beams heat treated by the *Thermowood*-process used at the time, with a process peak temperature of 220°C. The current process for Thermowood D has a peak temperature of 212°C and different circulation pattern for the saturated steam.

Reference preservative treatment

Two types of reference preservative treatment were used, full-cell impregnation with Wolmanit CX8 (from BASF/Wolman) to a retention of 12 kg/m³ (NWPC class AB level) and dip-impregnation with Laquin Seal from Becker-Acroma AB. The first preservative is a Copper-organic preservative in retention for Use Class 3 with copper(2)hydroxycarbonate, boric acid and bis-(N-Cyclohexyl-diazoniumdioxycopper as active ingredients. The latter preservative is a metal-free preservative for use in façade and window joinery (NWPC Class B) and consists of a water emulsion of organic biocides (triazols and 3-iodo-2-propynylbutylcarbamate) and an alkyd emulsion as binder.

Coating systems

ICP (Internal Comparison Product)

ICP is a solvent-borne red-pigmented semitransparent alkyd paint which is required as internal standard paint for EN 927-3 testing and its composition is exactly defined in the standard.

White alkyd paint

A solvent-borne white alkyd paint from Alcro-Beckers AB, *Front Täcklasyr*, was used. The solvents were: Tolyfluanide (<1%), semi-heavy aliphatic naphtha (25-50%) and xylene (1-5%). The pigments were mainly titanium dioxide.

White system paint (alkyd primer + acrylic top)

The primer was a SB alkyd, *Utomhusgrundfärg*, from Alcro-Beckers AB with titanium dioxide as pigment and aliphatic naphtha as main solvent. Other solvents in the primer were tolyfluanide and 2-Butanonoxime. The top coating was a water-borne acrylic latex paint, *Stugfärg*, with 1,2-benzisotiazol-3-(2H)-on, iodopropynyl-butylcarbamate and bronopol as fungicides and TiO₂ as pigment.

Brown semi-transparent acrylic paint (SB stain + WB acrylic top)

The priming SB dip-stain, Laquin Ton Brun SX/17002-452, from Becker-Acroma AB was used. The solvents in this stain were diethyleneglycol, butylglycol och sec-butanol. The acrylic laquer was a waterborne base, Laqvin Clear 30 EM 1472-0030, with an addition of a concentrated stain, Laqvin Ton Chestnut YZ1104-2930 (which consisted of red ferric oxide pigment, C:I Pigment Red 101) dissolved in diethylene glycol). The biocides in the acrylic laquer was a hydroxyphenylbenzotriazol derivative, 3-iodo-2-propynylbutylcarbamate and bis(1,2,2,6,6-pentamethyl-4-piperidyl)sebacate.

Tung oil

The Chinese tung tree oil coating system from Wibo Färg AB, consisted of a priming oil, Jupex 45, and a film-forming oil top, Jupex 90. Jupex 45 consisted of 50% Tung oil and 50% n-paraffin (C10-C13) and Jupex 90 of 50% Tung oil, 45% Linseed oil and 5% n-paraffin. None of the products contained any biocides.

Preparation of coated wood panels

The 20 x 100 x 375mm wood panels were coated, according to recommendations from the manufacturers, on the top face and the sides. The end-grain faces were sealed by a SB primer (*Utomhusgrundfärg* from Alcro-Beckers) and a long-chain alkyd paint, *Målarfärg* (from Alcro-Beckers). This top coat also covered 50mm and 25mm, respectively, of the top and side faces next to the end-grains. This leaves 300x100mm area on the top face (and two 20x300mm areas on the side faces) for evaluation of the coating on the wood substrate and prevents end-grain water suction and cracking starting from the end-grain.

The ICP was applied in three layers to a total amount of 150 g/m², as the standard prescribes. The white alkyd paint in two layers, to a total amount of 200 g/m²; the white system paint to a total of 100+160 g/m²; the brown acrylic paint to a film thickness of 75µm; the Tung oil system to a total amount of 100+20 g/m².

Additional sets of panels were given a water trap according to Annex F in EN 927-3. In this case a 25mm diameter hole was drilled through the top face to a depth of 5mm after the panels were coated as described above.

Field exposure

The samples were put out in March 2003 at 45° on rigs facing south in SP Träteks test field in Bogesund, approximately 40 km north-east of central Stockholm, Sweden (see figure 2).



Figure 2: Field exposure of coated panels according to EN 927-3 in the Bogesund field

Evaluation of the panels

After one year the first full evaluation of the panels was made according to EN 927-3. After another year an optical evaluation was made and samples of organisms on the panel surfaces were taken with MycoTape™. After 2.5 years another evaluation of the panels will be made to be presented at the conference.

The panels were evaluated regarding:

Degree of Mould and staining fungi growth

The rating scale of 0-5 according to EN 927-3 Annex C (referring to ISO 4628-5) and ASTM D3274-76 was used. The American standard prescribes microscopic identification of surface disfiguring type. MycoTape™ (tapelifts) were taken from the surface of the samples. The coverage of disfiguring fungi (in %) on the tape was evaluated and the organisms were identified by Mycoteam (Norway).

Degree of Blistering and Flaking

The rating scale of 0-5 for both categories, according to EN 927-3 Annex E and ISO 4628-2 and ISO 4628-5, respectively, was used.

Degree of Cracking

The rating scale of 0-5, according to EN 927-3 Annex E and ISO 4628-4 was used.

Degree of coating adhesion strength

The rating scale of 0-5, according to EN 927-3 Annex B and ISO 2409:1994 was used after cross-cutting with a razor-blade tool.

Degree of colour change

The colour change, ΔE^*_{ab} (deltaE), was measured according to the ISO-standard 7724-3, with a colorimeter. By use of a templet, six measuring points on each panel were taken on the same spots. The colour change, between each reference panel stored dark in climate room and the corresponding group of panels exposed in field, ΔE^*_{ab} , is calculated from the parameters L (brightness), a^* and b^* (chromatic coordinates). Brightness ranges from white (+) to black (-), a^* from red (+) to green (-) and b^* from yellow (+) to blue (-). ΔE^*_{ab} , which indicates the amplitude of the colour difference, but not how the actual colours differ, was calculated by equation 1 (Anonymous 1998):

$$\Delta E^*_{ab} = \sqrt{((\Delta L^*)^2 + (\Delta a^*)^2 + (\Delta b^*)^2)} \quad (1).$$

RESULTS AND DISCUSSION

EN 927-3 prescribes evaluation after one year of field exposure, and after such a short exposure time the performance mainly depends on the coating formulation and not so much on wood-coating interaction which will be decisive for the long term performance of the coated panels.

Degree of Mould and staining fungi growth

In table 1 the one-year performance regarding mould growth is shown. The difference between different coating systems is much greater than between different substrate groups. The internal comparison product (ICP) and the brown semi-transparent acrylic coating perform extremely well almost independent of wood substrate. The only traces of mould on the acrylic paint were easily removed by washing them (sponging in clean luke-warm water). The fungicides of the white alkyd paint were obviously less efficient than for the ICP and brown acrylic and slightly poorer than the white system paint. Already after 5 months exposure, most tung oil coated panels were moderately covered by mould and after one year there was very little if no trace of the oil coating and most panels were severely or totally covered by mould. However, the oiled furfurylated (see figure 3, top right group) wood panels had only traces of mould unlike the untreated or preservative treated wood panels. Also the oiled heat treated and acetylated panels were slightly less covered by mould than the controls.

Table 1: Degree of mould growth on the panels after one year in field, on a rating scale from 0 to 5

(where 0 means no fungal growth, 1: <5% coverage, 2: 5-10%, 3: 10-20%, 4: 20-40% and 5: over 40% coverage by mould or staining fungi).

Wood species	sap/heart	Treatment	Coating:				
			ICP	Alkyd	Alk+Ac	Acr	Oil
before wash							
Scots Pine	sapwood	untreated, control	0,0	1,5	1,0	0,0	4,0
	heartwood	untreated, High pinosylvin cont.	0,0		1,0	0,0	4,0
	mixed	Heat treatm (ThermoWood D)	0,0		1,0	0,0	3,0
	mixed	Acetylation	0,8		1,7	0,3	3,3
	sapwood	Furfurylation (VisorWood20)	0,2	1,2	1,0	0,3	1,3
	sapwood	Wolmanit CX8, 12 kg/m ³	0,2	1,0	1,0	0,0	4,3
Norway spruce	sapwood	Metal-free dip pres, class B	0,2	0,0	1,0	0,0	5,0
	mixed	untreated	0,0		1,0	0,0	
	mixed	Heat treatm (ThermoWood D)	0,0		1,0	0,0	
Siberian Larch	heartwood	untreated	0,0		1,0	0,0	2,0
European Oak	heartwood	untreated	0,0	1,7	1,0	0,0	3,0
after wash							
Scots Pine	sapwood	untreated, control	0,0	1,5	1,0	0,0	4,0
	heartwood	untreated, High pinosylvin cont.	0,0		1,0	0,0	4,0
	mixed	Heat treatm (ThermoWood D)	0,0		1,0	0,0	3,0
	mixed	Acetylation	0,8		1,0	0,0	3,3
	sapwood	Furfurylation (VisorWood20)	0,2	0,8	1,0	0,0	1,0
	sapwood	Wolmanit CX8, 12 kg/m ³	0,2	1,0	1,0	0,0	4,0
Norway spruce	sapwood	Metal-free dip preserv, class B	0,2	0,0	0,0	0,0	5,0
	mixed	untreated	0,0		0,0	0,0	
	mixed	Heat treatm (ThermoWood D)	0,0		1,0	0,0	
Siberian Larch	heartwood	untreated	0,0		1,0	0,0	2,0
European Oak	heartwood	untreated	0,0	1,7	1,0	0,0	3,0

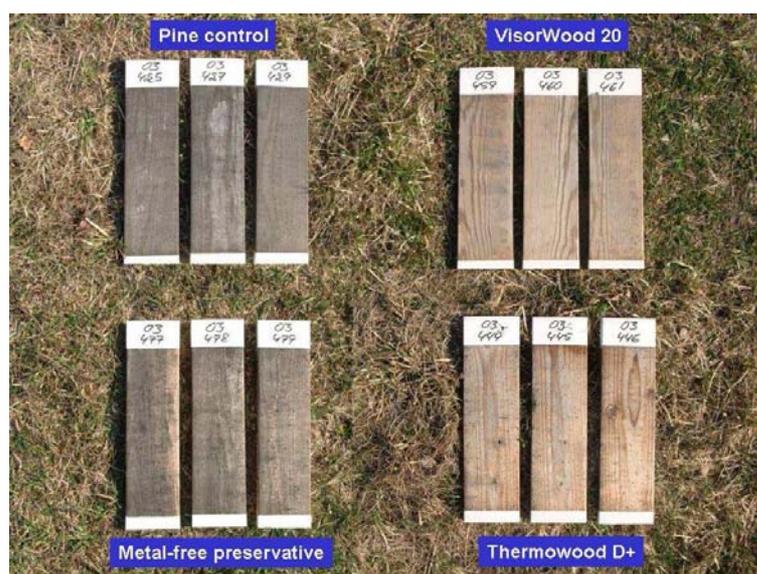


Figure 3: Test panels that were originally oiled after one year in field.

After another year (totally two years of field exposure), surface samples of the panels were collected with MycoTape for identification of disfiguring fungi. The results are shown in table 2. The panels coated with white alkyd paint were not included in this identification, since few substrate groups were included for this coating type. The quantification of the fungi is only related to the amount on the tape and does not reflect the actual coverage of the panels, i.e. the samples were generally collected from spots that seemed to be more covered than the rest of the panel area (in order to ensure the sufficient amount needed for identification) and sometimes the mould tend to stick poorer to the tape than to the coating. The disfiguring fungi that were identified were: *Hormonema dermatioides*, *Aureobasidium pullulans* and *Cladosporium* sp., and this was as expected due to previous studies of

disfiguring fungi on painted wood surfaces. *Aureobasidium pullulans* was exclusively isolated from materials coated with ICP, respectively from acetylated panels and on untreated Scots pine (control). *Cladosporium* sp. was predominantly isolated from the system paint (Alk+Acr), respectively furfurylated panels, ThermoWood D (spruce) panels and Cu-org. treated panels. Disfiguring fungi are morphologically different from each other, and these results might indicate that some specific species prefer one coating or wooden material prior to another.

Table 2. Identification and degree of mould growth / disfiguring fungi after 2 years in field. 10 treatments/controls and 4 coating systems. (X = samples are missing)

Coating→ Modification / wood species ↓	ICP	Alk+Acr	Acryl	Oil
ThermoWood D – pine	No fungal growth	c.f. <i>Hormonema dermatioides</i> <5%	X	X
VisorWood 20 pine	c.f. <i>Hormonema dermatioides</i> <5%	15-20%	c.f. <i>Hormonema dermatioides</i> 5-10%	<i>Hormonema dermatioides</i> 70-80%
Acetylated pine	cf. <i>Aureobasidium pullulans</i> <5%	X	X	X
ThermoWood D – spruce	No fungal growth	<i>Cladosporium</i> sp. <5%	No fungal growth	X
Control/Ref ↓				
Untreated Control Scots pine sapwood	cf. <i>Aureobasidium pullulans</i> <5%	<i>Hormonema dermatioides</i> <5%	No fungal growth	<i>Hormonema dermatioides</i> 70-80%
Cu-org pres (full cell impr.)	No fungal growth	<i>Cladosporium</i> sp., <i>Hormonema dermatioides</i> <5%	<i>Hormonema dermatioides</i> <5%	<i>Hormonema dermatioides</i> 80-100%
Metal free dip preservative	No fungal growth	No fungal growth	No fungal growth	<i>Hormonema dermatioides</i> <i>Cladosporium</i> sp. <5%
Larch heartwood	No fungal growth	No fungal growth	Blue stain (not identified) <5%	X
Oak heartwood	<i>Hormonema dermatioides</i> <5%	No fungal growth	No fungal growth	<i>Hormonema dermatioides</i> 80-100%
Pine heartwood (high Pinosylvin content)	cf. <i>Hormonema dermatioides</i> + algae <5%	c.f. <i>Hormonema dermatioides</i> <5%	No fungal growth	X

Degree of Cracking

The performance concerning cracking is shown in table 3. For the ICP, the cracking degree is generally very low. For the heat treated panels, spruce panels, pine heartwood and oak heartwood panels coated with ICP, there was no cracking at all. For the panels coated with the brown semi-transparent acrylic coating (Acr) most panels were crack-free, except for the preservative treated panels that were slightly cracked. The pure alkyd (Alkyd) and the system paint (Alk+Acr) performed similar to the pure acrylic, with very few panels with cracks. However the cracking of the oiled panels was quite extensive for most substrates. The exceptions were pine heartwood and acetylated panels with none or very little cracking.

Table 3: Degree of cracking of the panels after one year in field, on a rating scale from 0 to 5

Wood species	sap/heart	Treatment	Coating:				
			ICP	Alkyd	Alk+Ac	Ac	Oil
Scots Pine	sapwood	untreated, control	0,5	0,0	0,3	0,3	4,3
	heartwood	untreated, High pinosylvin cont.	0,0		0,0	0,0	0,0
	mixed	Heat treatm (ThermoWood D)	0,0		0,0	0,0	3,0
	mixed	Acetylation	1,5		1,0	0,0	0,7
	sapwood	Furfurylation (VisorWood20)	0,7	0,8	0,3	0,0	4,3
	sapwood	Wolmanit CX8, 12 kg/m ³	0,8	0,0	0,3	1,3	3,7
Norway spruce	sapwood	Metal-free dip pres, class B	0,8	0,0	0,7	1,0	3,7
	mixed	untreated	0,0		0,0	0,0	
	mixed	Heat treatm (ThermoWood D)	0,0		0,0	0,0	
Siberian Larch	heartwood	untreated	0,2		0,0	0,0	1,7
European Oak	heartwood	untreated	0,0	0,0	0,2	0,0	5,0

Degree of Blistering, Flaking, Adhesion strength and Colour change

The was no blistering or flaking of the coating film on the panels, except for some blisters on white alkyd on furfurylated wood and slight flaking of all coating types (except white alkyd) on the preservative-impregnated wood.

The adhesion strength was good (rating between 0.0 and 0.5) for all coating systems on all substrates.

The colour change, ΔE^*_{ab} , for the white alkyd was by far the highest for the oak heartwood panels and with furfurylated and preservative treated slightly higher than for the controls. For the white system paint and the semi-transparent coatings (ICP and brown acrylic), the colour change was negligible for all substrates. For the oiled panels the colour change was, as expected, depending on the starting colour – the darker brown the starting colour, the larger the colour change, i.e. the ThermoWood and furfurylated panels had the largest colour change values.

CONCLUSIONS

After only two years in field, it is difficult to make a relevant evaluation of the possible improved coating performance when modified wood substrates are used instead of unmodified. Especially, since the modified wood was not free of defects – thermally treated wood had knots in the evaluated surfaces and acetylated and furfurylated had cracks already before the field exposure.

However, a few conclusions can still be drawn:

- Tung oil is not suitable for coating of any wood substrates if a long maintenance interval is desired.
- Alkyd coatings are less suitable for substrates with lower surface pH (e.g. acetylated and furfurylated) than unmodified wood but gave good results with thermally treated wood.
- Acrylic coatings seem to be suitable for all modified wood substrates included but not for the reference preservative treated wood (due to cracking and flaking of the latter).
- None of the thermally treated wood panels, independent of coating system, developed cracks.
- The mould growth depends mainly of the coating formulation and not on the wood substrate. However, there was a strong reduction in mould growth on the oiled furfurylated panels compared to the other oiled substrates.

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NEW PROPERTIES FOR WOOD BY PLASMA TREATMENT

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Keywords: Coating, plasma, protection, water-repellency, wettability, wood

ABSTRACT

In textile industries, plasma technology is used to make fibres water-repellent: fluorinated monomers or silicone products polymerise under the effect of plasma. A invisible microfilm is created on the fibres, which are thus protected against water. The aim of this study is to transpose this technology to wood in order to make it waterproofed and to protect it when used outdoors. Different plasma treatments on bare wood and coated wood are presented: fluorine in gaseous phase, fluorine in liquid phase and silicone in gaseous phase. As the plasma coating is invisible, the unfinished and natural wood appearance so sought after by architects is retained when the treatment is applied to bare wood. Applied on coated wood, the treatment allows to extend the service life of the coating. By protecting wood from moisture, the micro-film has been envisaged as a barrier against brown rot fungi. But it has been shown that the plasma treatments do not provide any preventive protection against basidiomycetes.

INTRODUCTION

Wood is a remarkable material extensively used for construction and decoration. Like other biological materials, wood is susceptible to environmental degradation (Roux *et al.* 1988). When exposed outdoors, a complex combination of chemical, mechanical, biological, and ultraviolet and visible-light induced changes contribute to its weathering. Therefore, to ensure the long term value of wood substrates, they are usually coated with various decorative and protective finishes such as paints, stains or varnishes. Transparent systems are often used, because they allow the natural beauty of wood to remain visible. However, the durability of such transparent systems is limited. The most important degradations of an exterior wood coating come from the dimensional variations of wood, which strain the coating and lead to its cracking. Therefore, the durability of a wood-coating system could be increased through the stabilisation of these variations. Thermal or chemical treatments are effective, but most of them modify the surface characteristics and consequently the coating adhesion is no more guaranteed (Podgorski and Roux 1999). A better durability of the coating could be expected either in improving the wood-coating interface, or in protecting the wood-coating system from its main enemy, namely water.

Plasma treatments have been found to be very effective in modifying the surface properties of various polymers, such as their wetting behaviour (Xiao 1997). Plasma can be defined as a partially ionised gas, containing charged and neutral particles, including: electrons, positive or negative ions, radicals, excited atoms, and molecules (Kaplan and Rose 1991). The plasma species interact with solid-phase substances generating chemical and morphological changes in the very top layers

of the plasma-exposed substrates. The gas used has a major importance on the effects produced on the treated surfaces.

In the wood industry, the use of plasma technology may have two applications. The first one consists in increasing the wettability in order to expect a better adhesion of coatings and therefore a better performance of these coatings. In this case, gases such as oxygen, air, carbon dioxide can be used. The improvement of wood wettability by plasma treatments was previously studied at CTBA (Podgorski *et al.* 2000). The second one consists in decreasing the wettability to make wood water-repellent (Figure 1). This case considers fluorine-containing monomers or silicone-containing monomers that polymerise through the plasma leading to an invisible and water-repellent coating.

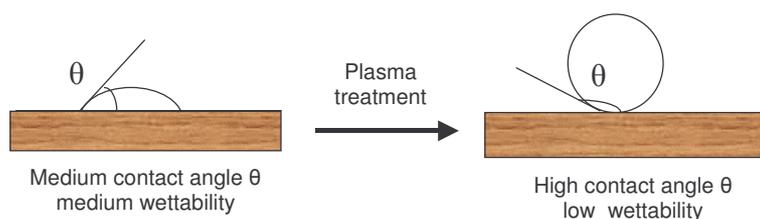


Figure 1: Water-repellency of wood through plasma treatment

In this second case, two strategies can be considered:

- if this new water-repellent coating turns out to be sufficiently weather resistant, it would be possible to apply the treatment directly on the bare wood. As the coating is invisible, the unfinished, natural wood appearance would be retained, at present highly appreciated by French architects;
- if the film is not sufficient in itself, its deposit on a coated wood might help to extend the service life of the traditional coating and ensure that wood will regain market shares for outdoor uses.

By protecting wood from moisture, the micro-film envisaged may act as a barrier against wood-destructive micro-organisms, and represent a new preservative treatment. This paper deals with the use of plasma treatment to make wood water-repellent and to develop new coatings for wood. Different plasma coatings on bare wood and coated wood are presented: fluorine in gaseous phase, fluorine in liquid phase and silicone in gaseous phase.

EXPERIMENTAL

Scots pine samples (150 mm x 74 mm x 18 mm) were used with an initial moisture content of 12 %. Plasma deposition in gaseous phase and in liquid phase was carried out at the IFTH. The treatment chamber is a vertical cylinder having a diameter of 45 cm and a height of 45 cm and therefore a volume close to 90 l. The upper part of the chamber is connected to a quartz tube in which the plasma is created thanks to a

micro-wave generator operating at 2450 MHz. Pumping is performed to ensure a water extraction from the material to be treated and therefore a good plasma quality. For plasma treatment with liquid phase, the monomers are sprayed (0.2 to 0.8 ml / sample) on wood samples which are then introduced into the plasma chamber.

In this study, different plasma coatings of wood surface to create water repellent characteristics are presented (Table 1): fluorine in gaseous phase (C_3F_6), fluorine in liquid phase (fluorinated acrylate with a C_8F_{17} chain denoted AC_8F_{17}) and silicone in gaseous phase (HMDSO).

Reduced water penetration into wood surfaces by deposition of tetrafluoromethane (CF_4) and perfluoromethane (C_3F_6) (Podgorski *et al.* 2000), hexamethyldisiloxane (HMDSO) or polymethyldisiloxane (Denes *et al.* 1999, Denes and Young 1999, Mahlberg *et al.* 1998), or butene (Magalhaes 2000) has already been reported. First experiments have shown that plasma treatments can be applied either to bare or finished wood (Podgorski *et al.* 2000).

Table 1: Nature of gas and liquid used for each treatment

Plasma treatment	Gas monomers	Co-Gas promoting reaction of polymerisation	Liquid monomers
Fluorine in gaseous phase	C_3F_6	CF_4	
Silicone in gaseous phase	HMDSO	O_2	
Fluorine in liquid phase		CF_4	AC_8F_{17}

An experimental design has been used to study the influence of the different treatment parameters on the wettability. The different treatment parameters that have been studied are:

- gas flow (20 to 80 cm^3/min)
- liquid monomer quantity (0.2 to 0.8 ml)
- power (700 to 1100 W)
- distance between samples and plasma source (37 to 57 cm)
- treatment time (1 to 15 min)
- frequency (20 to 50 Hz)

After plasma treatments, contact angle measurements have been made using distilled water drops of 5 μl . Five drops were used on each samples and a mean contact angle θ was calculated.

RESULTS AND DISCUSSION

Comparison of the different plasma treatments

Wood samples treated with the different plasma treatments exhibit very high water contact angle ($60^\circ < \text{contact angle} < 144^\circ$) in comparison to the unmodified samples (mean contact angle = 10°), indicating the creation of a hydrophobic surface (Figure 2). On one hand, treatments with fluorine monomers are more effective than treatment with silicone. On the other hand, a treatment in liquid phase gives better results than in gaseous phase. In liquid phase, some fluorine monomers probably penetrate into wood before polymerisation on the wood surface. This penetration in wood may explain better wood surface properties.

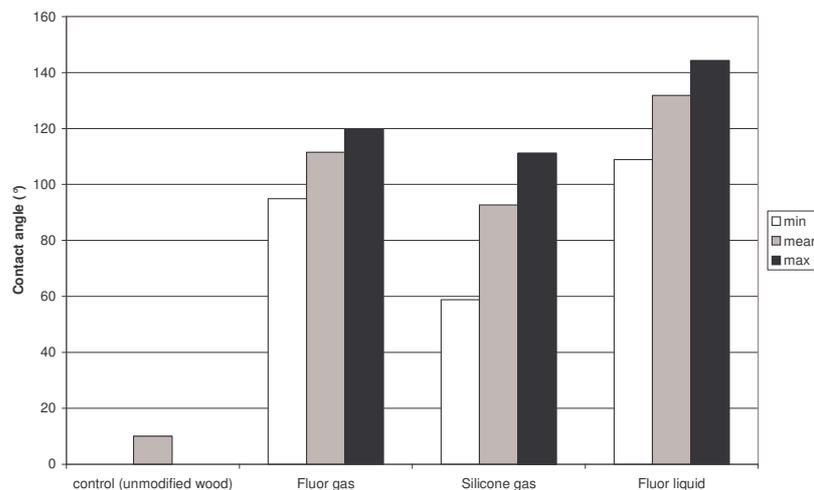


Figure 2: Comparison of the different plasma treatments on pine

The best treatment conditions have been determined for treatment in gaseous phase and treatment in liquid phase (Table 2).

Table 2: Best plasma conditions for pine treatment in liquid phase

Gas flow (CF ₄) (cm ³ /min)	Monomer quantity (AC ₈ F ₁₇) (ml)	Power (W)	Distance samples/ plasma source# (cm)	Treatment time (min)	Frequency (Hz)	Mean contact angle (°)
20	0.8	700	37	9	20	144.3

Influence of each treatment parameter on contact angle (treatment in liquid phase)

For the most interesting treatment (fluorine in liquid phase) the influence of each treatment parameter on contact angle has been studied by comparing the mean contact angle θ_h obtained with the high level of the treatment parameter and the mean contact angle θ_l obtained for the low level of the treatment parameter (Table 3). A positive difference $\theta_h - \theta_l$ means that the treatment parameter has a positive effect: the mean contact angle increases when the parameter level increases.

Power and frequency have negative effects on contact angles: the plasma treatment is less effective when performed at high power ($\theta = 125.3^\circ$ at 1100 W) than at low power ($\theta = 137.4^\circ$ at 700 W). Gas flow, monomer quantity, distance sample/plasma source and treatment time have positive effects on contact angle which are maximum when treatments are performed at the high level of these parameters.

Table 3: Influence of the different treatment parameters on contact angle (treatment in liquid phase)

	Plasma treatment parameters					
	Gas flow	Monomer quantity	Power	Distance samples/plasma source	Treatment time	Frequency
Low level	20cm ³ /min	0.2ml	700W	37cm	1min	20Hz
θ_i	129.2°	129.6°	137.4°	127.0°	130.3°	135.9°
High level	80cm ³ /min	0.8ml	1100W	57cm	9min	50Hz
θ_h	133.5°	133.1°	125.3°	135.7°	132.4°	126.8°
$\theta_h - \theta_i$	4.3°	3.5°	-12.1°	8.7°	2.1°	-9.1°
Effect of the parameter on θ	+	+	-	+	+	-

Interaction between the power and the distance 'samples/plasma source'

The power and the distance between samples and plasma source are linked (Figure 3). Contact angles are more important if distance and power are at their maximum or minimum at the same time. In other cases, plasma treatments are less effective.

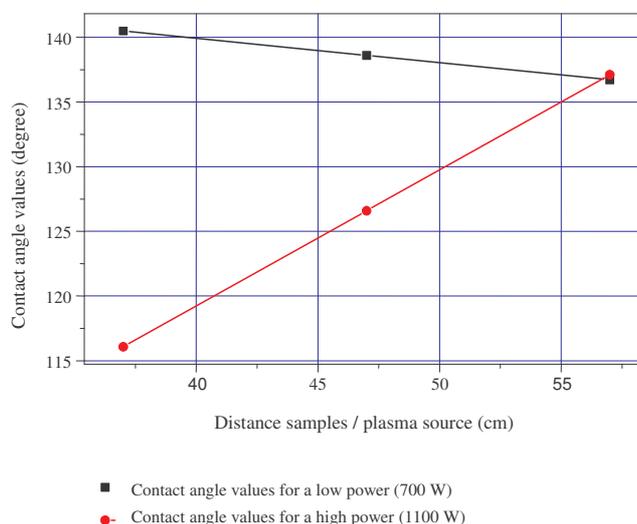


Figure 3: Interaction between the power and the distance sample/plasma source

The plasma treatment parameters leading to the highest contact angle have been determined (Figure 3 and Table 3) and are reported in Table 4. These theoretical conditions lead to contact angles higher than 144.3° that is to say to contact angles close to those obtained with Teflon®.

Table 4: Plasma parameters for an optimum treatment of wood (liquid phase)

Gas flow (CF ₄) (cm ³ /min)	Monomer quantity (AC ₈ F ₁₇) (ml)	Power (W)	Distance samples/ plasma source (cm)	Treatment time (min)	Frequency (Hz)
80	0.8	700	37	9	20

Influence of the wood moisture content on plasma treatment

Experiments have been carried out on wood samples with different moisture contents: vacuum dried, 6 %, 12 % and 18 % (Figure 4). For the treatment based on fluorine in gaseous phase, moisture has a negative effect on wood as observed for textiles. The plasma treatment is carried out under vacuum which leads to a water extraction. This water modifies the composition of the gas used and a competition between the plasma deposit and a surface degradation appears. It is known that fluorine blended with hydrogen (coming from the wood water) has a stripping effect. The plasma treatment with fluorine in liquid phase is not affected by the wood moisture content because the acrylate used is not miscible with water. Therefore, the vapour water coming from the wood samples has little influence on the results. The plasma treatment made with silicone is not influenced by the water coming from the wood samples. This treatment is based on $C_6H_{18}OSi_2$ and O_2 and already contains a lot of hydrogen and oxygen. Therefore the dilution with water vapour does not affect its composition.

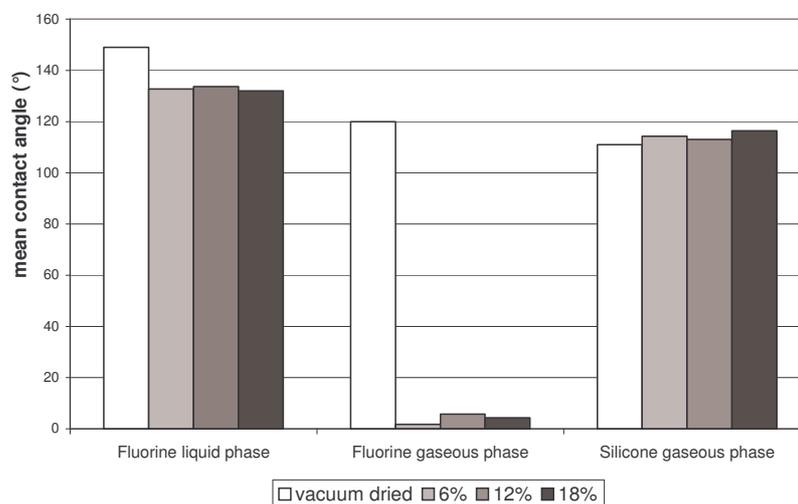


Figure 4 : Influence of the wood moisture content on the plasma treatments

Plasma treatments and artificial weathering

The artificial weathering of plasma deposition on bare wood and coated wood has been studied on meranti samples. Plasma treatments based on silicone in gaseous phase and on fluorine in liquid phase have been applied to bare wood samples and to some wood samples coated before the plasma treatment. In this case one set of samples was coated with an alkyd stain, and another set was coated with an acrylic stain. Then, the different samples have been exposed in artificial weathering on a Gardner wheel for 6 weeks. After the 6 weeks and as expected, the bare wood samples without any plasma treatment turn grey due to the effect of water and UV radiations. The plasma treatment is interesting since the grey colour is less pronounced with the silicone treatment, and especially with the fluorine treatment. On coated samples, the fluorine treatment is once again the most interesting, since the little damage that could be seen with the alkyd stain on samples without plasma treatment are not present with the plasma treatment.

Some samples have been re-exposed in artificial weathering for another 6 week period. After these 12 weeks, the fluorine treatment is the most effective. The effect of this treatment is especially visible in the middle

of the samples. In this experiment and to be able to treat all faces of the samples, a special rotating equipment has been used in the plasma chamber. By using this equipment, the middle of the sample was closer to the plasma source than the rest of the samples, which explains a better water-repellency in the middle. After these 12 weeks, the fluorine treatment is also effective on the acrylic stain since no degradation at all are present, whereas the coated samples treated with the silicone plasma treatment show as much degradations as the control non plasma treated.

Plasma treatments as a protection against fungi

The effectiveness of two plasma treatments (silicone gaseous phase and fluorine liquid phase, used with the best treatment conditions) against wood destroying basidiomycete fungi have been studied. Tests have been carried out according to ENV 839 'Wood preservatives-Determination of the protective effectiveness against wood destroying basidiomycetes-application by surface treatment' (May 2003). Other tests have also been performed according to another standard which is not used anymore within CEN/TC 38. After 16 weeks of exposure to *Coniophora puteana*, *Gloeophyllum trabeum* and *Poria placenta* according to ENV 839 and after 12 weeks of exposure to *Coniophora puteana* and *Poria placenta* according to the other standard, no effectiveness of the plasma treatments was observed.

CONCLUSIONS

The aim of the study was to transpose the plasma technology to wood - a technology that is currently well mastered in the textile industry. The considered application of plasma treatment consists in decreasing the wood wettability in order to make it water-repellent. Applied on bare wood and because this film is invisible, the unfinished, natural look of the wood, currently so sought-after by architects, is retained. Test samples of pine were waterproofed by gaseous fluorine or silicone plasma treatment and liquid fluorine plasma treatment. The water wettability tests attest to the effectiveness of these treatments. Treatment parameters best suited to bare wood were selected. Artificial weathering tests on bare wood samples and coated wood samples with and without plasma treatments have shown that best results were obtained in liquid phase. Plasma treatment based on fluorine in liquid phase delays the weathering of bare wood and coated wood. Better results could probably be obtained by making a selection of treatment parameters directly on coated wood samples. Plasma treatments do not provide any preventive protection against basidiomycetes. This kind of treatment may have different applications in the wood industry. For example it could be considered for coated wooden windows to better protect some pieces particular sensitive to weathering like window sills and bottom beads.

ACKNOWLEDGEMENTS

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INVESTIGATION OF PURE AND PLASMA TREATED SPRUCE WITH SURFACE ANALYTICAL TECHNIQUES

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Keywords: Dielectric barrier discharge at atmospheric pressure; electron spectroscopy; metastable impact electron spectroscopy; plasma; ultraviolet photoelectron spectroscopy; wood; x-ray photoelectron spectroscopy

ABSTRACT

Surface properties of wood can be changed using a dielectric barrier discharge at atmospheric pressure. Depending on the utilised gas, the surface tension and chemical activity can be increased or hydrophobic surfaces can be obtained by plasma-polymerisation. For characterising the altered wood surfaces, different electron spectroscopic methods are used. XPS or ESCA is a well known technique for analysing the chemical composition of wood surfaces. UPS and MIES are largely unknown methods on cellulosic materials. As UPS reflects the Density Of States (DOS), MIES the Surface Density of States (SDOS) respectively, these methods are useful to characterise changes of wood surfaces based on plasma treatment. It is shown that these techniques yield indeed reproducible results and, in particular, possess the potential to give information on the interaction of molecules with wood surfaces.

INTRODUCTION

During recent years, plasma technology has become more and more important and has expanded into various technical fields. For generating light, cleaning, surface coating, creation of special functional groups or where fundamental adhesion problems occur, plasma technology is an all-rounder. Yet up until now its full potential has not been fully tapped. By use of plasma-treatment, surfaces are cleaned, heated and activated. Thereby, the surface is influenced by electrons, ions, molecules and radicals, which by direct pulse transmission remove impurities. Chemical reactions also reduce impurities and generate special functional groups. As a result of these systematically generated groups or the destruction of chemical bonds, the surface tension and chemical activities increase. In this way surface properties can be modified without influencing the volume characteristics (Hippler *et al.* 2001). A new innovative application of plasma technology is the treatment of sensitive, organic materials such as timber.

As a result of temperature sensitivity, large dimensions and vacuum unsuitability, the renewable resource wood caused problems in the technical realisation and was not satisfactorily treatable. The treatment has now be facilitated by a dielectric barrier discharge (DBD) and a particular, customised setup. By plasma-treatment prior to any coating, process wood and derived timber products can be conditioned in such a way that coatings (paints, lacquers, glues) will be absorbed quicker and the levels of adhesion will increase. Thus, the fracture strength of laminated wood can be increased significantly and a reduction of the

amount of required glue is feasible. Even with only a slight percentage reduction a substantial cost saving can be achieved, in addition to a decrease in the environmental pollution levels. Another conceivable application could be the partial abandonment of frequently used primers. Furthermore, the utilisation of new materials and material combinations will be possible. Newly-made materials are the wood-plastic-compounds. Investigations have proven that plasma-treatment can completely solve many problems of varnishing. Due to the fact that no visual alteration on the surface occurs by plasma-treatment, this technology is applicable on surfaces where the aesthetic character needs to be preserved. Because gas temperatures are less than 100°C a thermal influence through pyrolysis is excluded; rather a slight heating can improve the quality of adhesion additionally (Rehn *et al.* 2003, Rehn and Viöl 2003, Rehn *et al.* 2004). Hydrophobic surfaces are obtained by plasma-polymerisation under atmospheric pressure utilising gases such as methane, ethane and silane-mixtures. These water repellent layers can substitute the conventional, protective coatings (Bente *et al.* 2004).

In order to optimise the plasma-treatment and used coatings, glues *etc.* basic investigations need to be carried out. If the fundamental effectiveness and modification of wood surfaces are understood, the parameters of treatment and coatings can be altered for achieving optimal results. To investigate surface properties and modifications X-Ray Photoelectron Spectroscopy (XPS), Ultraviolet Photoelectron Spectroscopy (UPS) and Metastable Impact Electron Spectroscopy (MIES) have been applied to clean, untreated and plasma-treated spruce surfaces.

The traditional preservation by means of coating and impregnation, as well as the adhesion, can be optimised in durability and in function by the plasma-treatment. With the plasma-treatment the quality of wood and derived timber products is improved, thereby heightening competitiveness relative to other materials.

EXPERIMENTAL

The ultrahigh vacuum (UHV) apparatus is evacuated by a combination of a turbo molecular and a ion getter pump. The base pressure is better than 5×10^{-11} mbar which is achieved after bake-out to 150°C for at least 24 h. It is equipped with a commercial Low Energy Electron Diffraction (LEED) system (LEED Electronics PHI Model 11-020), a commercial X-ray source (Specs RQ-20/38C) for X-Ray Photoelectron Spectroscopy (XPS), providing Mg K_{α} or Al K_{α} with photon energies of 1253.6 eV and 1486.6 eV, respectively. These photons hit the sample surface under 80° to its normal. Metastable Impact Electron Spectroscopy (MIES) and Ultraviolet Photoelectron Spectroscopy (UPS) are performed applying a combined source which provides He 2^3S atoms (excitation energy 19.8 eV) and HeI photons (excitation energy 21.2 eV). The source is schematically shown in Figure 1. Besides ground state He the cold cathode discharge produces He 2^1S , He 2^3S , HeI and He⁺ in the source chamber. The He beam is formed by a skimmer between source and buffer chamber. He⁺ ions are removed from the beam by a condenser inside the buffer chamber.

Within the source, a He partial pressure of about 10-20 mbar is necessary. The source chamber provides a He pressure of about 1.5×10^{-3} mbar, the buffer chamber $1 \cdot 10^{-5}$ mbar. Inside the UHV chamber

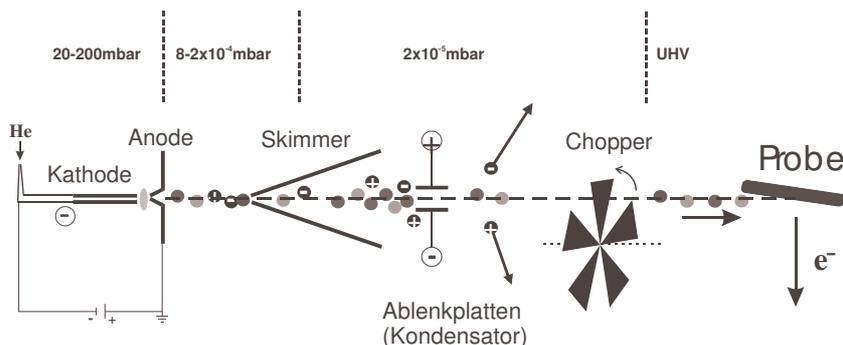


Figure 1: Schematic representation of the combined He⁺/HeI source

the He partial pressure rises to about 3×10^{-9} mbar. This does not affect any measurement because He is unreactive. He⁺ and HeI are separated from each other by a time-of-flight chopper system. By applying separation electronics and a two-channel counter system, MIES and UPS are measured simultaneously. He⁺ atoms and HeI photons hit the sample under 45° to surface normal. Electrons emitted under 90° by photons or metastable atoms impact on the sample are analysed by a hemispherical analyzer (VSW HA 100). The acquisition of all spectra is computer controlled. MIES and UPS spectra are measured under normal emission within 100 s. XPS spectra are measured under 10° with respect to the surface normal within 2-3 h, typically, depending on resolution requirements. The sample position within the UHV chamber is adjusted by a commercial system (Aerotech UNIDEX 11) under computer control. This guarantees a high reproducibility.

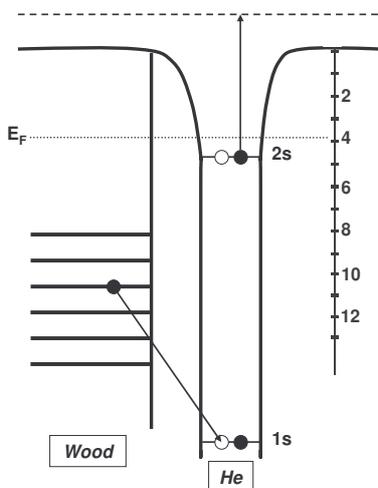


Figure 2: Schematic representation of the Auger de-excitation process in front of an insulating surface

The principles of photo electron spectroscopy (UPS and XPS) are well known. Briefly, photon impact on the surfaces results in the emission of electrons with characteristic energies (Ertl and Küppers 1985). XPS provides information on the chemical composition while UPS in principle shows the Density of States (DOS) averaged over about 15 Å depth. In the energy range between the Fermi level and less than 20 eV which is corresponding to the valence band. In MIES, He⁺ atoms, most of them in He⁺2³S states, approach the surface with thermal velocity. Interaction takes place at distances between 3Å and 10Å from the surface on the impinging trajectory with the very outermost surface wave functions (Harada *et al.* 1987, Morgner 2000). Therefore, MIES is extremely sensitive for surface states. This is important for the study of the interaction of water molecules with the surfaces presented here. In principle three different processes occur during the interaction of He⁺ with surfaces depending on the surface work function, its conductivity and its possible coverage with molecules. Because of the insulating nature of the surface under study, only Auger de-excitation (AD) is observed in the investigations presented in this contribution. Therefore we restrict our description of the interaction on this process. Figure 2 shows the interaction process schematically. The He⁺ atom approaches the surfaces. As soon as the overlap between surface wave functions and the He 1s orbital becomes significant, a surface electrons fills the He 1s vacancy, thus emitting the electron in the He 2s state.

This electron carries the excess kinetic energy E_{kin} . The energy balance is similar to the one for UPS with a different excitation energy E^* (19.8 eV instead of 21.2 eV):

$$E_{kin} = E^* - E_B - \phi \quad (1)$$

Hereby ϕ denotes the surface work function and E_B the electron binding energy with respect to the Fermi level. The spectral distribution $N(E)$ reflects the Surface Density of States (SDOS) which is responsible for the surface interaction with impinging atoms or molecules from the ambience.

For the plasma treatment of the wood surfaces, a prototype of a plasma reactor was developed in order to meet several industrial applications. Figure 3 shows the set-up for an industrial application (Viöl 1999, 2002, 2004). The speed of the wood motion can be varied between 3 m/min and 18 m/min. Timber materials up to a thickness of 30 mm and a width of 150 mm can be treated and are guided through two vertical movable pairs of electrodes. As a result, the wood can be treated from both sides simultaneously. In order to get a homogeneous discharge the gas gap has to be held constant at 2 mm. This is realised by rollers running over the wood surface. In order to chill the electrodes, to collect and destroy generated ozone and to homogenise the discharge, air is drawn centrally through the two pairs of electrodes. A high voltage generator, with a 30 kHz, 20 kV AC output, is connected to each pair of electrodes, which are placed under and over the wood. Whilst the wood is grounded, a phase shift of 180° among the two pairs of electrodes induces a potential difference of 40 kV. With this arrangement, power densities over 25 W/cm^3 are realised. With a discharge width of $2 \times 30 \text{ mm}$, the treatment times vary between 0.2 s and 1 s. The oval form of the electrodes, the consistent air flow and the exact alignment of the wood between the upper and the lower electrodes lead to a nearly homogeneous discharge without hot filaments. In order to treat single, small, specimens for XPS, UPS and MIES, it was required that a cavity was milled into a large plank where this small specimens were deposited. The wood specimens were prepared of 0.1 mm thick splinters, which can be produced by a planer. Out of these splinters the specimens for the measurements were cut.

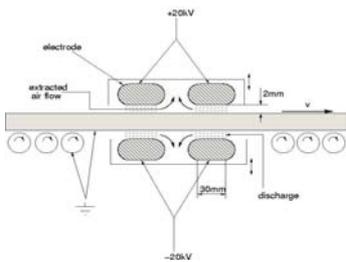


Figure 3: Schematic sketch of the plasma discharge set-up

RESULTS AND DISCUSSION

Figure 4 shows XPS survey spectra of spruce surfaces which are untreated, treated in silane (SiH_4) plasma and treated in synthetic air plasma from the top to the bottom, respectively. The experimental details of the plasma treatments are described in the experimental section. The spectra are shown as a function of the binding energy.

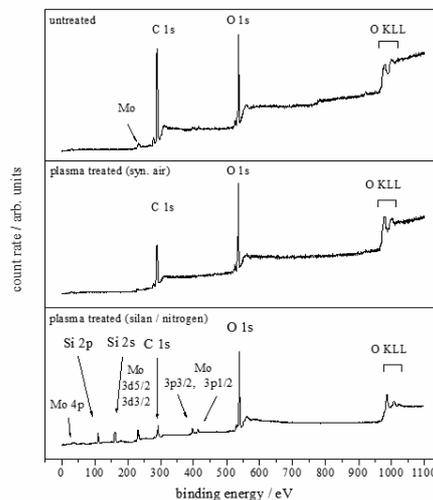


Figure 4: XPS spectra of spruce which are treated in silane (SiH_4) plasma, untreated and treated in synthetic air plasma, respectively

The untreated spruce surface mainly shows C(1s) and O(1s) peaks at binding energies E_B of (288.6 ± 0.3) eV and (536.1 ± 0.3) eV, respectively. The peak ratio O(1s)/C(1s) amounts to 0.32. A decomposition of the C(1s) peak into its 3 components C_1 (C-C), C_2 (C-O) and C_3 (C=O) will be made in a forthcoming publication. Additional structures around $E_B \approx 233$ eV, 397 eV and 416 eV are due to emission from the sample holder made of molybdenum. These structures do not affect the following discussions. The surface treated in synthetic air plasma also shows two main structures: C(1s) at $E_B = (288.6 \pm 0.3)$ eV and O(1s) at $E_B = (535.2 \pm 0.3)$ eV. The C(1s) peak position fits very well with the untreated surface while the O(1s) peaks position is shifted to lower binding energies by 0.9 eV. The peak ratios O(1s)/C(1s) amount to 0.57. This is significantly higher than for the untreated surface which means, that a significant amount of oxygen must be adsorbed on or incorporated into the spruce surface. The surface treated in a plasma containing silane also shows more than two structures. C(1s) is found at $E_B = (287.6 \pm 0.3)$ eV and O(1s) at $E_B = (536.3 \pm 0.3)$ eV. The C(1s) peak position and the O(1s) peak position fits well to the ones for the air treated surface. The relative peak ratios O(1s)/C(1s) amount to 5.1. This is even significantly higher than for the air treated surface and is due to the partly SiO₂ covered surface. Besides the small Mo contribution two additional peaks at $E_B = (106.4 \pm 0.3)$ eV and $E_B = (157.8 \pm 0.3)$ eV occur. These are due to emission from Si(2p) and Si(2s), respectively. The further enhanced oxygen uptake compared with the other spruce surfaces, together with the incorporation of silicon, suggests, that during silane plasma treatment a Si-O complex is formed. Figure 5 shows UPS spectra of spruce surfaces treated in the same manner as described with Figure 4. During UPS / MIES measurements the surface was kept at 130°C. Prior to the studies the surface was carefully dehydrated by heating at 100°C under UHV conditions until the QMS water signal has reduced to less than 5 percent of its original value. In auxiliary experiments to be described in our forthcoming publication, we have verified that we do indeed study the wood surface, not adsorbate water, segregating to the surface.

The surface work function (WF) can be estimated from the low-energy offset of the spectra (4.4 (± 0.1) eV for untreated and air treated surfaces and 4.7 (± 0.1) eV for the silane treated surface). All spectra show a gap of about 3.1 (± 0.1) eV between valence band maximum (VBM) and the Fermi level (corresponding to the binding energy $E_B = 0$ eV). The band

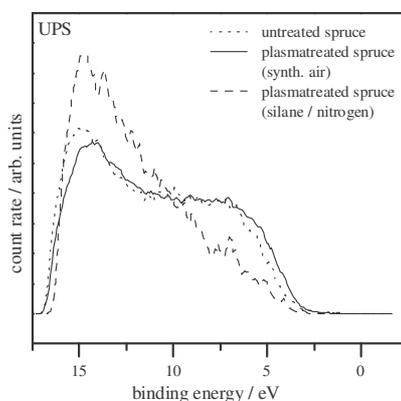


Figure 5: UPS spectra of spruce surfaces which are treated in silane (SiH₄) plasma, untreated and treated in an synthetic air plasma, RESPECTIVELY

gap amounts to 3.1 eV (VBM)+4.4 eV(WF)=7.5 eV for the untreated and

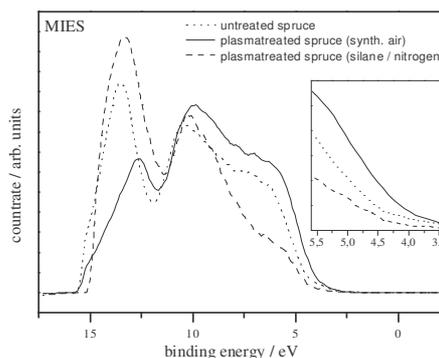


Figure 6: MIES spectra of spruce surfaces which are treated in silane (SiH_4) plasma, untreated and treated in a synthetic air plasma, respectively

air treated surfaces and 7.8 eV for the silane treated surface. All UPS spectra are relatively unstructured. The spectrum of the silane-treated surface is quite different from the both others, which are very similar to each other. The XPS results suggest a Si-O-formation on the surface which is however not confirmed by the UPS results. The main change of the Bulk Density of States (BDOS), in the region accessible to UPS, for the silane treated surface is a strong reduction of the intensity up a binding energy of 10 eV and an increase of the band gap.

Figure 6 shows MIES spectra of the surface characterised in Figure 4 by XPS. The MIES spectra are induced by the Auger De-excitation process, because the MIES and UPS spectra show comparable band gap widths. The spectra are dominated by a strong emission between 12 eV and 14 eV and a broad structured emission between 3 eV and 12 eV. The MIES spectra directly reflects the SDOS of the surface which is responsible for any electronical interaction between surfaces and impinging molecules. Inspection of Harada *et al.* 1997 and Günster *et al.* 1999 shows that the MIES spectra are typical for surfaces terminated by carbohydrates and/or hydroxyl groups whereby the emission between $E_B=5$ to 10 eV can be attributed to C(2p) derived molecular orbitals (MOs), while that for $E_B>11$ eV is due to C(2s) derived MOs. Emission in the region around $E_B=6$ eV may also come from the ionization of O(2p) MOs. Summarising, we have shown that the combination of XPS, UPS and MIES can be applied to the study of the surface of untreated and plasma-treated spruce and yields reproducible results. In future work we will study the interaction of water with well-characterised wood surfaces by applying the same combination of techniques.

ACKNOWLEDGEMENTS

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NEAR INFRARED SPECTROSCOPY ASSAY FOR THE BIOTECHNOLOGICAL MODIFICATION OF WOOD

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Keywords: Brown rot, *Ceriporiopsis subvermispora*, fibre optic probe, FT-NIR, lignin, white rot,

ABSTRACT

White rot and brown rot fungi have been identified as potential biotechnological tools to change the properties of wood surfaces and of sound wood. Extensive screening programs were carried out in the past to identify the most active fungal isolates. The screening targets, used by most scientists, were loss of weight and quantification of specific wood components including lignin, as well as cellulose and hemicellulose sugars by wet lab chemical methods. These methods are time consuming and require a lot of technical skill in order to achieve reliable results. Usually, wood blocks were inoculated with the fungal cultures and assayed after 2-3 months. Using near infrared spectroscopy (NIR), changes in the chemical composition of solid spruce or beech wood samples or wood samples after milling can be reliably detected after several days of cultivation with the fungi. The linear correlation of the NIR lignin signal with the results obtained from wet-lab analysis is significant for beech and spruce wood. The sensitivity of the NIR spectroscopic lignin determination of wood meals exceeded that of the conventional Tappi standard methods. The determination of the lignin content using an NIR fibre optic probe directly on wood surfaces is quick, sensitive, non-destructive, easy to apply and sensitive enough to be suitable as a screening method for fungi of technological interest.

INTRODUCTION

The biodegradation of lignocellulose is the domain of wood rotting fungi. Most of them are basidiomycetes. Brown rot fungi degrade cellulose and hemicelluloses of softwood leaving the lignin more or less undegraded but strongly modified, whereas white rot fungi are able to mineralise all wood constituents simultaneously. However, some selective white rot fungi can remove lignin in preference to cellulose, an ability that makes these fungi interesting for the industrial production of cellulose. The composition and the properties of wood are changed by all of these fungi. However, conventional methods to determine the lignin content of wood are very time consuming and make it difficult to handle large numbers of samples (TAPPI T 222 om-88). Standard deviations of the TAPPI standard method range from 0.4 % w/w to

1.6 % w/w lignin (Schwanninger and Hinterstoisser, 2002). The limited number of replicate analyses together with relatively high standard deviations restricts the sensitivity of the method. Therefore, in screening programs for technologically interesting species and strains, the determination of the lignin content of wood samples after fungal decay is carried out after several weeks of colonisation by the fungi, although the treatment time in the technological process may be much shorter.

Near infrared (NIR) techniques have been shown to be powerful and rapid tools for the determination of wood components (Gierlinger *et al.* 2002a, 2002b, 2004, Bailleres *et al.* 2002, Yan and Krishnagopalan 2003, Yeh *et al.* 2004, Easty *et al.* 1990, Schultz and Burns 1990) and chemical changes associated with the brown-rot biodegradation of spruce wood (Kelley *et al.* 2002). Absorption bands observed in the reflectance spectra of wood arise from overtones and combination bands of vibrations of C-O, O-H, C-H, and N-H which have their fundamental molecular absorption in the mid infrared (MIR) region. Various constituents give similar absorption signals leading to highly overlapping bands, with the exception of substance classes such as aromatics, which can be directly related to the amount of lignin (Michell and Schimleck 1996, Osborne and Fearn 1998, Shenk *et al.* 2001).

Materials and methods

Fungal strains

Ceriporiopsis subvermispora CBS 347.63 (Selective white rot), *Trametes versicolor* (Simultaneous white rot on beech, selective on spruce), and *Gloeophyllum trabeum* (brown rot), which had been pre-cultivated on malt extract agar plates, were used in this study.

Cultivation of fungi on wood

Veneers

Spruce or beech wood veneers (3 cm x 5 cm x 0.1 cm) were steam sterilised for 15 min and soaked for a few seconds in 2 % (w/V) corn steep liquor (CSL, Agrana) containing suspended fungal mycelium (one malt extract agar plate overgrown by the fungus was mixed in 150 ml 2 % (w/V) sterile corn steep liquor in a Waring blender for 30 s at full speed) before they were put in agar dishes (9 cm diameter) with 25 ml water agar (1.5 %) and beech tooth picks to allow growth of the fungi throughout the whole wood surface in a moisture-saturated atmosphere. The samples were incubated at 30°C in plastic bags. The moisture content of the samples after incubation was 150 – 200 %. After the treatment, the mycelium was washed from the surface and the samples were dried at 50°C for several days.

Wood shavings

Wood shavings (100 % moisture content, 5 g based on oven-dry weight) were steam sterilised for 15 min and inoculated with 5 ml of a mycelium suspension, as described above, and were cultivated at 30°C in a moisture saturated atmosphere. The moisture content of the cultures was 200 %. After the treatment, the samples were dried at 50°C and milled with a Retsch Ultra Centrifugal Mill ZM 1000 with a fixed ring sieve with 80 µm hole width and again oven-dried at 50°C.

FT-NIR-spectroscopy

After cooling down to ambient temperature, FT-NIR spectroscopy was performed on a Bruker FT-IR spectrometer (Equinox 55) equipped with a NIR fibre optic probe and a germanium-diode detector giving a spectral range from 10000 cm^{-1} to 5100 cm^{-1} . Spectralon, a thermoplastic resin, was used as a reference. An area of about $9\text{-}10\text{ mm}^2$ was analysed with the fibre probe being in close contact with the sample. 100 scans per measuring area were collected at a spectral resolution of 10 cm^{-1} . Ten areas per veneer were taken at random positions on the front and back side of the veneers.

For the short time cultivation with white rot fungi (Figure 4), the measuring areas were not taken at random positions, but the same five spots on the veneer were measured before the sterilisation of the veneer and after the treatment with the fungal culture.

Data analysis

The second derivatives of the spectra were calculated with the Bruker OPUS-NT software (Version 5) using the Savitzky and Golay algorithm by means of a 17 smoothing points filter. Analyses of variance of the data obtained from the NIR spectra were carried out with the Design Expert software (Version 6, StatEase, Inc. Minneapolis, USA, <http://www.statease.com>).

RESULTS AND DISCUSSION

NIR-spectra

Figure 1(a) shows typical NIR reflectance spectra from spruce and beech wood meals. The absorption region between 6020 and 5770 cm^{-1} is attributed to the lignin compound of wood, showing bands of vibrations deriving from the aromatic ring (C-H) as well as C-H vibrations of methyl groups and methylene groups respectively (Schwanninger and Hinterstoisser 2001, Schwanninger *et al.* 2004). To accentuate differences between the spectra, they were transformed into the second derivative mode (Figure 1(b)).

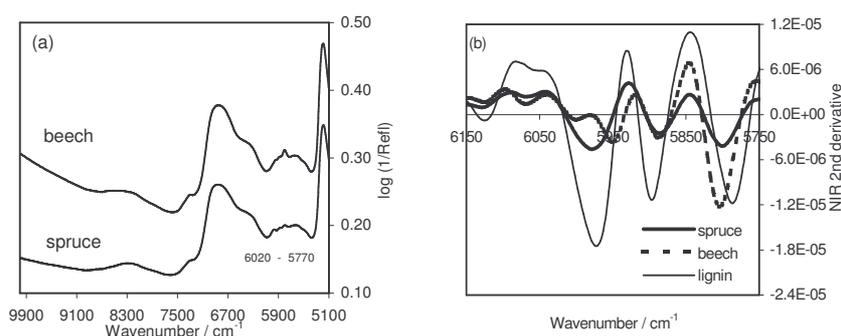


Figure 1. FT-NIR reflectance spectra of beech and spruce wood meals (a) and 2nd derivatives of NIR spectra of spruce, beech, and Klason lignin from beech.

The lignin content of the sample can be calculated from the amplitude of the minimum near 5980 cm^{-1} . Additionally, lower lignin contents shift the minimum near 5800 cm^{-1} and 5980 cm^{-1} to higher wavenumbers and the amplitude minimum near 5890 cm^{-1} to lower wavenumbers (Schwanninger *et al.* 2004). The 2nd derivative of the NIR spectrum of spruce shows a high similarity to that of lignin but with a lower

intensity and different ratios of the amplitudes, additionally accompanied by small shifts. In beech wood however, the amplitude near 5980 cm^{-1} is influenced not only by the lignin content of the wood sample, but also by the beech xylan. C-H deriving bands of the acetyl groups show minima in the second derivative spectra near 6000 cm^{-1} , 5955 cm^{-1} , 5890 cm^{-1} , and near 5805 cm^{-1} . Thus, in hardwood, the amplitude at 5980 cm^{-1} is not a minimum; it is a local maximum between the two minima deriving from acetyl groups. The lignin content of beech wood samples is determined from this local maximum of the second derivative spectrum, if the xylan content is not changed too much or to a similar extent (Fackler *et al.* unpublished).

Lignin content of wood meals

The lignin content of spruce wood shavings that were modified by the selective white rot fungus *C. subvermispora* was assayed with the NIR method. For that purpose reflectance spectra from wood meals that were prepared from the samples were recorded. Figure 2 shows the amplitudes of the NIR spectra in the second derivative mode at 5978 cm^{-1} . The error bars indicate the 95 % confidence interval for the mean value obtained from eight replicate spectra. The differences of the amplitudes refer directly to the relative changes in lignin content from day to day. Schwanninger *et al.* (2004) calibrated the NIR-method with the wet-lab method for spruce wood and found a linear correlation ($R^2 = 0.956$) between 23 and 32 % w/w total lignin content (Equation 1).

$$L = -2.568 \text{ E}+06 * A + 14.41 \quad (1)$$

L Lignin content [% w/w]
A Amplitude [NIR 2nd derivative at 5978 cm^{-1}]

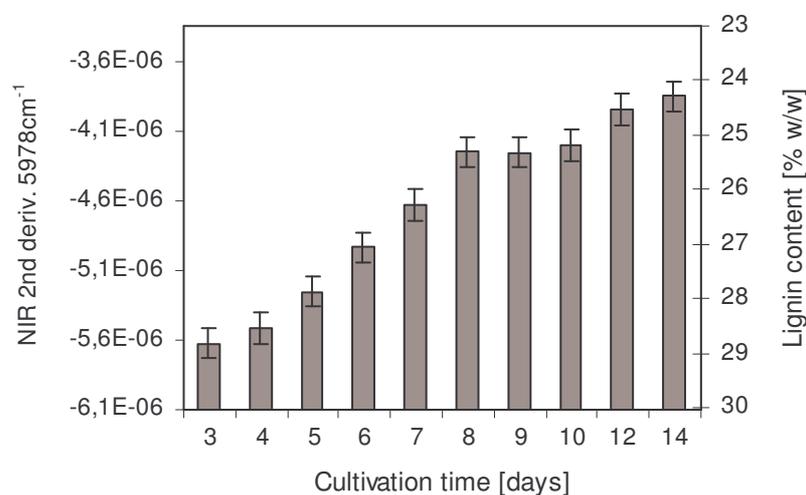


Figure 2: Amplitude of the 2nd derivative of the spectra of meals from white rot modified spruce wood shavings. Error bars indicate the 95 % confidence interval for the mean values.

Differences of amplitudes at 5978 cm^{-1} representing a difference in lignin content of 0.54 % w/w (twice the 95 % confidence interval of the mean value) can be reliably resolved by the method. The lignin content of spruce subjected to the selective white rot of *C. subvermispora*

decreases significantly during the first two weeks of cultivation and can be reliably detected after five days. Differences between the consecutive cultivation days 4 to 8 are significant as well, whereas the lignin decreases more slowly from day 9 to 14. Lignin degradation by *C. subvermispora* correlates well with the excretion of the lignin modifying enzyme manganese peroxidase (Fackler *et al.* 2003).

Lignin content of wood surfaces

Figure 3(a) shows the 2nd derivative of NIR spectra of surfaces of beech wood samples which had been subjected to wood rotting basidiomycetes for ten weeks. The biggest difference occurred again near 5980 cm⁻¹: selective white rot fungi (*C. subvermispora*) decrease the amplitude indicating a decrease of the lignin content. Simultaneous white rot (*T. versicolor*) led only to minor changes of the spectrum and thus the lignin content, although the weight loss of the sample exceeded 50 %. Due to the degradation of cellulose and hemicelluloses, the lignin content of brown rotted wood (*G. trabeum*) is higher than in the reference sample. The amplitude near 5800 cm⁻¹ is lower for all three fungi, indicating the degradation of beech xylan. A similar picture is presented in Figure 3(b), which shows the surface spectra of spruce wood subjected for ten weeks to selective white rot and brown rot. Changes of the amplitudes and spectral shifts indicate changes in lignin content caused by the fungi.

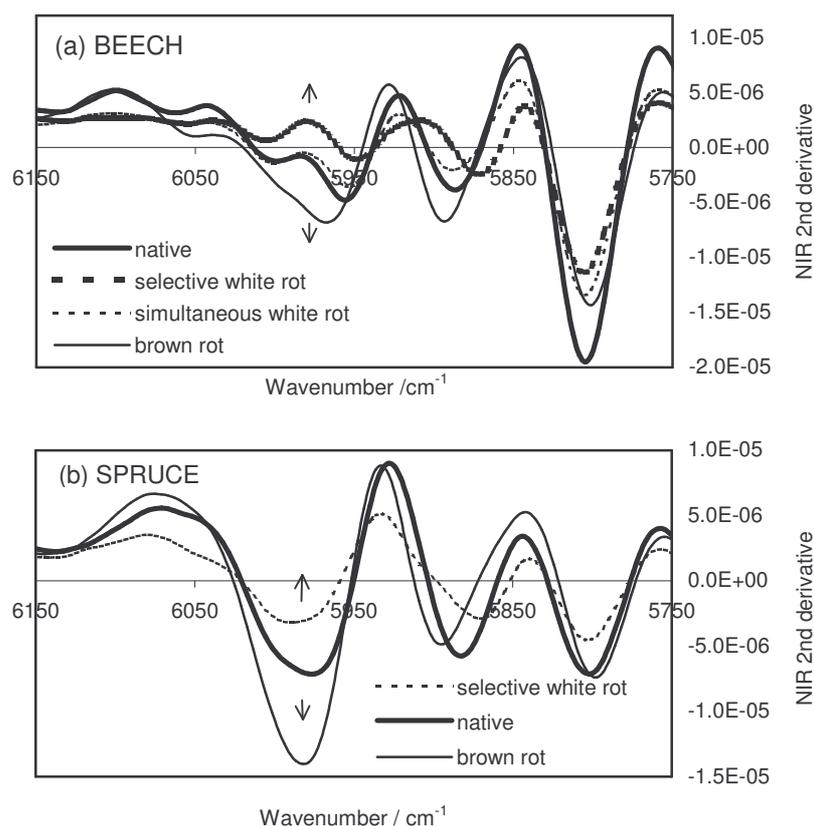


Figure 3: 2nd derivatives of NIR spectra of brown and white rot degraded wood surfaces. (a) beech and (b) spruce.

As described above for spruce wood meals, the NIR 2nd derivative at 5978 cm⁻¹ of the veneer surface is linearly correlated to the lignin content of an evenly modified wood sample or of the wood surface in early decay stages (Fackler *et al.*, unpublished results). Depending on the

metabolism of the species, the changes in the surface spectra can be detected already after several days. Figure 4 shows the differences in the NIR 2nd derivative amplitude of spruce veneers treated with the white rot fungi *C. subvermispora* (Cs), and *T. versicolor* (Tv) (which degrades lignin selectively on softwoods). Lignin attack by the first fungus is significant already after five days, whereas that of the latter is just above the limit of detection after five days and can be clearly measured after 10 days. It is hard to determine this small difference between these two white rot species by means of conventional techniques. Figure 5 shows the change of the amplitude of *C. subvermispora* treated wood surfaces during ten weeks and the corresponding estimated lignin loss.

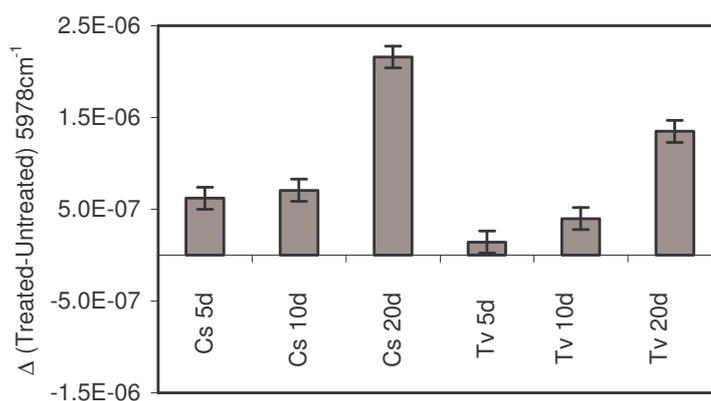


Figure 4: NIR 2nd derivative amplitudes of spruce wood surfaces subjected to two different white rot species (*C. subvermispora* – Cs and *T. versicolor* –Tv) for up to twenty days. Differences between treated and untreated veneers were determined. Error bars indicate the 95 % confidence interval of the mean values.

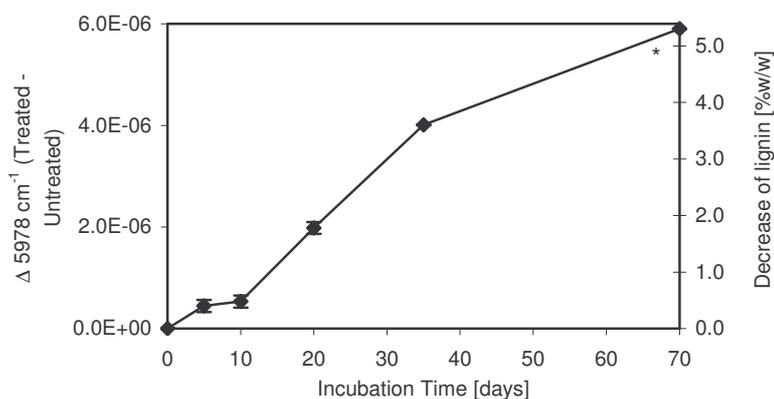


Figure 5: Change of the NIR 2nd derivative spectra of spruce wood surfaces modified by the selective white rot fungus *C. subvermispora*. (*) 70 days treatment is outside the calibrated range.

CONCLUSIONS

NIR spectroscopy is a quick and sensitive tool in order to estimate or determine the lignin content of wood after biotechnological modification by brown or white rot fungi. The amplitude of the 2nd derivative of the NIR spectra near 5980 cm⁻¹ is linearly correlated to the lignin content determined by wet-lab methods. Differences representing a lignin content smaller than 0.6 % w/w can be reliably detected from spruce wood samples.

Therefore, small changes during short bio-modification times of only a few days, small differences between fungal strains, and even changes during short time fermentations can be determined.

Unlike with the standard methods, samples are not destroyed for the analyses, and apart from drying and milling (if required), no sample preparation is necessary. Using a fibre optic probe, NIR spectra can be recorded directly from the surfaces of wood samples or wood meals. Many spectra can be recorded in one day (one spectrum per minute), and – if required – automatization of the method is possible.

ACKNOWLEDGEMENTS

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PARTICULARITIES IN AGAR BLOCK TESTS OF SOME MODIFIED WOODS CAUSED BY DIFFERENT PROTECTION AND DECAY PRINCIPLES

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Keywords: Basidiomycetes, EN 113, mass loss, moisture content, oil treatment, resins, silane

ABSTRACT

This paper introduces new test designs for modified wood and shows limitations of the established ones. One test allows for the quantification of mass loss plus strength loss under EN 113 conditions and the other can test the decay of wood particles and fibres. Three examples of wood modification show where EN 113 can cause false evidence - hydrophobicisation with oil, surface treatment with functional silane and cell wall treatment with formaldehyde containing resins. Oil or biocide treated EN V807 stakes in Kolle flasks incubated with *C. puteana* showed 30-40 % mass loss after five to seven weeks in the controls, when oil treatments just started to decay. Sixteen weeks of incubation could not distinguish between delayed decay and improved durability. EN 113 samples treated with 20 % functional silane ended up with 1-2 % mass loss and moisture contents between 95 and 121 %, after 16 weeks with *C. puteana*, *G. trabeum* or *P. placenta*. Although the experiments prove that the moisture content results from fungal action, and is not caused by passive water logging these results cannot be validated following EN 113 guidelines. Depending on the concentration, silane treated specimens depressed decay in the neighbouring controls. But test pairs with controls of less than 20 % decay are invalid according to EN 113 rules. Treatments with formaldehyde containing resins of solid wood blocks (EN 113) and wood particles (EN 113 related fibre test) showed comparable effects after attack by brown or white rot fungi. The hygroscopicity of resin treated wood particles (120-291 % moisture content in agar controls) was completely removed by hot water extraction. Results show that fungi regulate moisture up and down in these samples - with or without decay. Supplements to EN 113 are discussed to overcome its limitations.

INTRODUCTION

At the Institute of Wood Biology and Technology (www.holz.uni-goettingen.de) various wood modification methods have been under development for several years. Some of them also have the ability to improve the resistance against wood destroying fungi. In the last decades, the durability of wood treated with conventional biocides has been tested following the European Standard EN 113. This test uses the mass loss of solid wood blocks as criteria for decay and can be regarded as basis for the evaluation of durability due to wood decaying basidiomycetes. The wood modification systems, however, are not based on biocidal action. And for selecting modifying agents for further process development, more detailed information about the biological resistance of this material is needed than mass loss only. Therefore, new test designs or at least another interpretation of the test data produced by EN 113 could be necessary for the following reasons:

- Hydrophobicisation with oils, paraffins or waxes creates a high weight gain. Is mass loss in this case a result of decayed wood or decayed hydrophobic agent?
- Screening of new modification agents could be more convenient and informative in wood fibres and particles than in solid wood blocks.

Two new test designs were developed following EN 113 as closely as possible. One test allows for the determination of mass loss plus strength loss in an EN 113 environment, and the other one tests the decay of wood particles and fibres. Furthermore, the work contributes to a new interpretation of moisture content in wood samples. Basidiomycetes can transport water and nutrients over long distances (Jennings 1984). We want to focus attention on EN 113 fungi like *Coniophora puteana* and *Trametes versicolor* which transport water from the agar (93.5% bound water) to treated and untreated samples by colonising their substrates. The new test designs and/or conventional EN 113 are applied to three examples of wood modifications with hydrophobicising oil, functional silane and cell wall modifying resins causing problems in the evaluation of durability with standard methods. Small supplements to EN 113 are discussed, to avoid that substances are either evaluated to good or tests of agents with an exceptional mode of action have to be declared invalid.



Figure 1: Kollé flask with *C. puteana* and ENV 807 samples (four oil-treated, four controls)



Figure 2: Wood particles in stainless steel bags in polystyrene Petri dishes (lid removed) with *C. puteana*. Modified particles in upper bags – controls in lower bags

EXPERIMENTAL

Agar block tests according to EN 113

Decay tests with functional silanes (1, 5, 10 and 20 %) and formaldehyde containing resins (30 %) exactly followed EN 113 guidelines. Kollé flasks were used as containers with 50 ml malt agar medium (4 % malt extract, 2.5 % agar). Each flask contained one treated and one control sample (50 x 25 x 15 mm³, sapwood of *Pinus sylvestris* or *Fagus sylvatica* respectively) on stainless steel spacers. Three brown rot fungi *Coniophora puteana* (BAM Ebw.15), *Gloeophyllum trabeum* (BAM Ebw. 109), *Poria placenta* (FPRL 280) and one white rot fungus *Trametes versicolor* (CTB 863 A) were tested. After 16 weeks mass loss and moisture content were measured.

EN 113 agar block tests with a new sample design

In decay tests with hydrophobicising oil, a sample size was used in a time course study which allows the measurement of mass loss and strength loss.

In all modifications with high weight gains, mass loss can be a matter of decaying the modifying agent and not the wood. Decay of the latter will lead to mass loss and to strength loss. In each Kollé flask eight stakes sized like in ENV 807 (100 x 10 x 5 mm³) were positioned by stainless steel spacers in such a way that four treated samples and four control samples were assembled alternating and crosswise in two layers (Figure 1).

The total substrate volume is 40 cm³ in one flask and thus comparable to two EN113 samples (37.5 cm³) at a 2.6 times wider surface. Twelve samples each were harvested after an incubation period of 1, 2, 3, 4, 5, 7, 9, 12 and 16 weeks respectively. Prior to measuring mass loss, samples were soaked with tap water for 30 min under vacuum (10 kPa) and left

overnight, before measuring the dynamic modulus of elasticity (MOE) with a Grindosonic.

Testing modified wood particles under EN 113 conditions

In a screening phase of modifying agents, the testing of wood fibres and particles is a useful tool because they are easier to infiltrate and offer a wider surface for fungal attack. Inert mesh bags of an appropriate size that keep the material together as one sample and allow fungi to grow in and out are the key to such a test. Wood particles, as are used in the upper layer of particle board, were stuffed in stainless steel bags with a mesh size of 64 μm to a weight of 1 g dry matter per bag. Four of these bags (two with modified particles and two controls) were placed in pairs on stainless steel supports opposite each other (Figure 2) in polystyrene Petri dishes (143 x 22 mm²) containing 50 ml malt agar (4 % malt extract, 2.5 % agar).

Wood particles were modified with two different formaldehyde containing resins in three concentrations (30, 50 and 70 %) and aliquots were extracted with hot water in a Soxhlet apparatus (12 hours at 100°C). Bags were harvested after eight weeks of incubation. Mycelia were wiped off the bag surface and bags then were immediately weighed and dried at 103°C for 24 hours.

All Kolle flasks and Petri dishes were incubated in a climate room under EN 113 conditions (70 % +/- 5 % relative humidity, 22°C +/- 2°C).

RESULTS AND DISCUSSION

Hydrophobicising oil treatment and delayed mass loss

A common question with regard to the evaluation of hydrophobicising agents in agar block tests is if durability measured during the test period is a this stable effect, or due to the circumstance that fungi in an oil saturated environment need a longer time to establish themselves, thus just mimicking durability of the treated wood. The EN 113 test design with eight cross linked ENV 807 stakes comparing an oil and biocide treatment in a time course gives an answer to that question.

Whereas, measurable decay by *C. puteana* in treatments started after a lag phase of five to seven weeks, untreated controls show 30-40 % mass loss at that time (Figure 3). With 25 % mass loss after 16 weeks, oil treated samples still perform better than the controls with 65 % mass loss do, but compared to the biocide treated samples with zero mass loss, this oil treatment is classified as 'not durable'. Such a lag phase seems to be fungus specific, as *G. trabeum* in the same trial started decay earlier and more continuously (not shown in this paper).

Compared to mass loss, the measuring of MOE (Figure 4) emerges as the more sensitive tool for detecting wood decay. There is a strong increase in MOE loss in the controls from the first to the fifth week, reaching more than 80 % after the seventh week as a maximum value. This corresponds to the continuous rise of mass loss in the controls (Figure 3). In the oil treatment, the rise in MOE loss is continuous too, from the beginning up to 55 % after 16 weeks, but it does not correspond to the clear lag phase in mass loss. This implies that penetration of the oil treated sample by fungal hyphae might be

accompanied by another biochemical decay process leading to strength loss, than that one which is leading to mass loss afterwards.

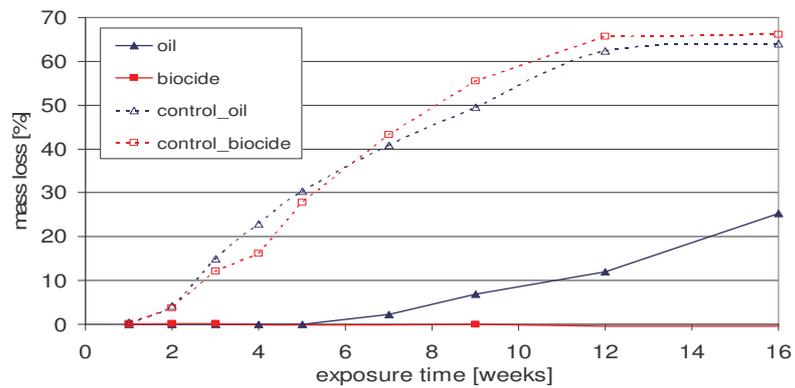


Figure 3: Mass loss caused by *C. puteana* of oil or biocide treated samples (n=12) and adequate controls in an EN 113 test with eight ENV 807 samples per Kollé flask

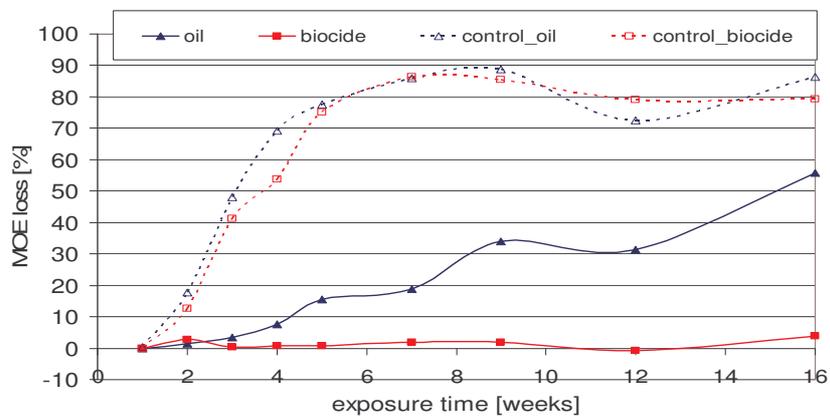


Figure 4: Loss of MOE caused by *C. puteana* of oil or biocide treated samples (n=12) and adequate controls in an EN 113 test with eight ENV 807 samples per Kollé flask

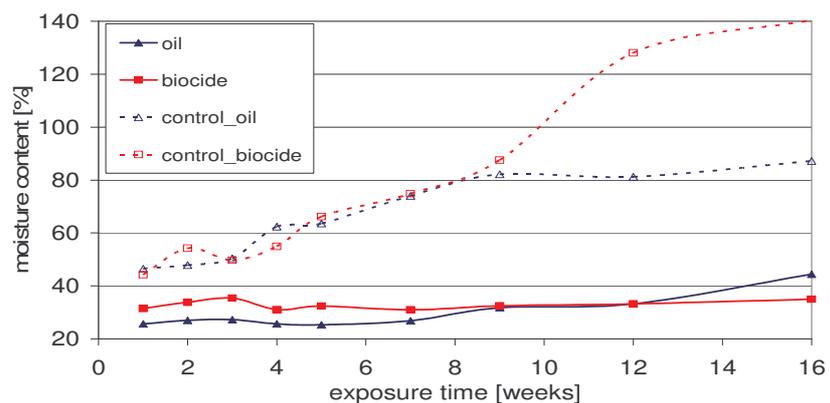


Figure 5: Moisture content caused by *C. puteana* in oil or biocide treated samples (n=12) and adequate controls in an EN 113 test with eight ENV 807 samples per Kollé flask

On the other hand, this experiment shows clearly that the mass loss in oil treatments is due to wood degradation. A degradation of oil only would produce no loss in MOE (Treu *et al.* 2003). Decay in oil treated samples starts at moisture contents of less than 30 % (Figure 5) and

does not exceed a moisture content of 45 %, at 25 % mass loss after 16 weeks. The same mass loss is achieved in the controls after four weeks but at a moisture content of more than 60 %. This indicates that moisture uptake of the samples is not correlated to the decay rate.

Another implication could be that *C. puteana* needs less water in a hydrophobic milieu than in pure wood. In biocide treated samples, there is no decay and the moisture content in the samples does not exceed 35 %. In the corresponding controls, decay is not affected by the treatments – neither by oil nor by biocide. Samples end up at 65 % mass loss. But the moisture content differs clearly. After nine weeks, the controls incubated together with biocide treatments take up more water intensively whereas the controls with oil partners do not. Both end up in a relation of 87 % to 140 % moisture content respectively.

If we regard the crosswise layered samples as one spatially staged substrate body with protected and non treated areas we can assume that a rise in moisture content of samples without adequate mass loss is due to an active water transport of the fungus into substrates which are not decayed.

Water management of fungi attacking samples treated with functional silanes

Samples treated with 20 % functional silane (Donath 2004) only showed 3.2 % or less mass loss after 16 weeks (Table 1). None of the three tested fungi (*C. puteana*, *G. trabeum* and *P. placenta*) could decay these samples but there is a clear dose response relationship to the used concentrations. Even 1 % silane showed in each fungus an effect on mass loss, but *G. trabeum* was most sensitive with 1.1 % mass loss at a 5 % concentration.

After EN 84 treatment, the silane treated samples were not hygroscopic with 30 % moisture content. Nevertheless, all samples treated with 20 % silane and incubated with *C. puteana* showed the highest moisture contents in this test (98.8 – 121.4 %), higher than the adequate controls (79.3 – 86.3 %) or the virulence controls (80 %). Thus indicating that *C. puteana* actively moistens the samples without hardly any decay. This contradicts the often used argument that fungi cannot decay because of too wet samples (water logging).

Regarding EN 113 guidelines (8.6.3 validity of the results) these results are invalid because those samples have more than 80 % moisture content at less than 3 % mass loss. In this case of 20 % functional silane and curing temperatures of 60°C and 103°C respectively (results shaded grey) tested against *C. puteana*, EN 113 excludes an effective treatment.

Table 1: Mass loss and moisture content of silane treated pine sapwood samples (n=6) and controls after 16 weeks incubation with *C. puteana*, *G. trabeum* and *P. placenta* according to EN 113

functional silane		EN 84 + EN 113 moisture content (mc) and mass loss (ml)							
		brownrot fungi						controls	
curing temperature °C	silane conc. %	C. puteana		G. trabeum		P. placenta		agar	
		mc	ml	mc	ml	mc	ml	mc	ml
treated samples									
20	20	121,4	3,2	–	–	–	–	30,5	–
60	20	115,3	0,6	–	–	–	–	33,8	–
103	20	98,8	-2,6	35	1,2	28,2	0,6	30,1	–
103	10	63,8	17,6	32,9	0,8	31,7	3,6	29,8	–
103	5	63,7	30,2	34,5	1,1	53,8	27,7	29,5	–
103	1	78,2	44,3	53,9	27,7	94,2	34,8	29,3	–
controls									
20	20	86,3	63,5	–	–	–	–	30,5	–
60	20	83,3	63,7	–	–	–	–	33,8	–
103	20	84,8	64,0	68,4	32,2	50,7	1,6	30,1	–
103	10	79,3	61,5	66,7	33,4	49,3	0,8	29,8	–
103	5	81,6	59,3	70	32,1	79,3	19,9	29,5	–
103	1	80,5	49,0	71,2	22,5	65,5	25,3	29,3	–
103	0	80	52,7	61,2	44,4	90,1	39	30,3	0,8

The same silane concentration at a curing temperature of 20°C gives a valid result in spite of the highest moisture content of 121 % because mass loss is 3.2 %. This limitation by a certain moisture content / mass loss ratio was set by experience with classical wood protecting agents with strong hygroscopic properties but does not reflect biological conditions like they arise in testing new wood protecting systems.

The control samples, *i.e.* those samples lying closely to the treated one in one common Kolle flask are clearly affected by their neighbours, with the silane treated samples. This “neighbourhood effect” is different for each tested fungus. *C. puteana* benefits from silane treatment of the neighbour samples as mass loss in the controls is higher (59.3 – 64.0 %) than in the virulence controls (52.7 %) which have no treated neighbours. There is a tendency, the higher the silane treatment concentration the higher the mass loss of the corresponding controls. *G. trabeum* is depressed in the decay of the controls (22.5 – 33.4 %) compared to virulence controls with 44.4 % mass loss. *P. placenta* shows a depression of control decay too but this depression is clearly concentration dependent, like the mass loss of the treated samples was – the lower the silane concentration of the treated samples the higher the mass loss of the controls. But as 10 % and 20 % silane treatments give results with less than 20 % mass loss in the controls (shaded grey) these results have to be regarded invalid again according to EN 113 guidelines.

Here EN 113 again leads to a wrong result because this 20 % limit cannot differentiate between originally poor growth or inhibited growth of the test fungus by the treated neighbour sample. Nevertheless it has to be stated that one mycelium in one Kolle flask can transport metabolites or non reacted substances from treated to untreated samples or can take them up from the gaseous phase after diffusion thus generating the so called ‘neighbourhood effect’.

Formaldehyde containing resins – species specific regulation of sample moisture content

Active moistening of a sample without mass loss and ‘neighbourhood effects’ occur with formaldehyde containing modifications too (Table 2).

Table 2: Influence of four basidiomycetes on moisture content and mass loss of resin treated samples in two EN 113 tests with and without leaching by EN 84 run by two independent laboratories.

formaldehyde containing resin			EN 113 - moisture content (mc) and mass loss (ml)											
			brownrot								whiterot			
			C. puteana		G. trabeum		P. placenta		T. versicolor		C. puteana		T. versicolor	
n	lab	% mc	% ml	% mc	% ml	% mc	% ml	% mc	% ml	% mc	% ml			
treatment	5	1					98	1	80	1				
		2					119	4	67	3				
treatment + EN84	5	1	96	0	67	0	37	1	59	1				
		2	112	1	52	0	68	2	61	4				
controls	5	1					53	6	55	36				
		2					58	61	46	33				
controls + EN84	5	1	80	64	61	42	46	7	57	36				
		2	103	66	56	44	61	63	53	41				
virulence controls	10	1	79	54	61	33	74	53	49	32				
		2	73	45	53	42	63	53	53	32				
agar controls	8	2	77	3					53	1				

not tested
mc > 80 % ml < 3%
Kontrollen < 20 %

This test was run parallel in two different laboratories using the same material. *C. puteana*, *P. placenta* and *T. versicolor* moisten the samples to more than 80 % at less than 3 % mass loss – again invalid results by EN 113 guidelines. *P. placenta* and *T. versicolor* produce less moisture in the treated samples with leaching by EN 84, but the mass loss values are comparable low (1 – 4 %). This proves that moisture exceeding 80 % is not the reason for hardly any decay. *C. puteana* produces still high moisture contents in the samples in spite of EN 84 treatment. Controls in *C. puteana* flasks benefit from the treated neighbour samples, whereas controls in *P. placenta* flasks do and do not. Although *P. placenta* isolates from both laboratories are equal in provenance and virulence (53 % mass loss in the controls) one isolate reacts very sensitively to the treated neighbours and the other one does not. Can fungi change their sensitivity towards chemicals?

Modified wood particles and fungal water management

Wood particles have the same fine structure like solid samples but their surface is about 250 times larger. Therefore, testing modified wood particles intensifies the described effects. Table 3 shows samples without water extraction having a high concentration dependent hygroscopicity (120-193 %). But *C. puteana* humidifies 30 % and 50 % samples, whereas 70 % samples are dehumidified. As there is no decay in any of these samples and the corresponding controls show mass loss even at higher moisture contents (225 % - 258 %), moisture is not the limiting factor for decay but the effect of the treatment. This is underlined by the hot water extracted samples with a low hygroscopicity (24 % - 26 %). Here the fungus moistens both treated samples and controls but the controls are no longer that strongly affected by the treatments. Mass loss in virulence controls was 25 % (extracted 43 %) and for solid wood samples (30 x 10 x 5 mm³) in the mesh bags 32 % (pine sap wood) and 39 % (beech).

Table 3: Moisture content (mc) and mass loss (ml) of resin2 treated wood particles (1g per mesh bag) with and without hot water extraction after eight weeks incubation with *C. puteana*.

Coniophora puteana		% mc	%ml	ml	% mc	%ml	ml	% mc	%ml	ml
samples		30 % resin 2			50 % resin 2			70 % resin 2		
treatment	n 6	176	1		196	1		153	2	
	STDEV	12	1		10	1		13	1	
control	6	231	9	0	222	12	1	258	22	3
	STDEV	32	4		30	13		26	19	
agar control	8	120	1,60		149	1,24		194	1,03	
	STDEV	4,14	0,61		10,48	0,45		7,88	0,21	
		30% resin 2 extracted			50% resin 2 extracted			70% resin 2 extracted		
treatment	n 6	124	2		84	1		93	-1	
	STDEV	38	3		8	2		9	1	
control	6	107	45	4	86	39	6	91	34	4
	STDEV	39	21		19	16		34	18	
agar control	8	25	0,75		24	0,53		26	1,19	
	STDEV	1,63	0,52		0,70	0,33		2,13	0,64	

Table 4 shows results of a treatment with resin type 3 which makes the samples even more hygroscopic (174 % - 291 %). Except the 30 % controls *T. versicolor* dehumidifies treated and control samples to 148-165 %. In case of the treated samples, this is an example that fungi also can dehumidify without decay. Hot water extraction of the samples removes hygroscopicity, controls are no longer affected by treatments but there is no decay in treated samples. At a comparable decay rate (29-47 % mass loss) *T. versicolor* moistens the controls about 120 % more proving that an increase in moisture content is not the result of a reciprocal mass loss but a fungal specific regulation of the water balance in the decayed substrate.

Table 4: Moisture content (mc) and mass loss (ml) of resin3 treated wood particles (1g per mesh bag) with and without hot water extraction after eight weeks incubation with *T. versicolor*.

Trametes versicolor		% mc	%ml	ml	% mc	%ml	ml	% mc	%ml	ml
samples		30 % resin 3			50 % resin 3			70 % resin 3		
treatment	n 6	162	3		165	1		148	3	
	Stabw.	34	2		55	0		36	0	
control	6	207	18	2	155	2	0	203	16	2
	Stabw.	81	19		31	3		63	13	
agar control	8	173,68	0,76		217,79	1,68		291,20	2,24	
	Stabw.	2,46	0,81		5,22	0,55		8,12	1,15	
		30% resin 3 extractet			50% resin 3 extractet			70% resin 3 extracted		
treatment	n 6	145	4		115	1		99	1	
	Stabw.	36	3		14	2		22	3	
control	6	228	32	4	282	47	6	227	29	3
	Stabw.	53	14		77	14		73	22	
agar control	8	30,79	0,45		27,27	0,79		26,75	1,10	
	Stabw.	1,10	0,64		1,24	0,76		0,97	0,82	

CONCLUSIONS

In tests with hydrophobicising agent's prolonged test periods are necessary to differentiate between durability and moisture caused delayed decay. In a hydrophobic environment, fungi can decay at comparatively low substrate moisture. The results with resins and silanes assume that brown and white rot fungi do regulate their substrate moisture. High moisture of samples can be a fungal strategy to overcome unfavourable decay conditions by diluting soluble fractions of preservative or modification products. EN 113 is a very useful and

reliable agar block test for biocides and this work shows that this applies to modified woods too. But several supplements have to be discussed:

- a prolonged test period of 22 weeks in the case of testing hydrophobing agents
- obligatory leaching treatment like EN 84 prior to EN 113 for all modifications
- the exclusion of samples with more than 80 % moisture content at less than 3 % mass loss is valid, if the agar controls have more than 80 % moisture too
- the exclusion of control samples with a mass loss of less than 20 % is only valid if there is no concentration dependent effect from treated samples to control samples (neighbourhood effect)

Furthermore, EN 113 performed with ENV 807 stakes has proved to be a very useful and more sensitive tool to measure mass loss and strength loss in one test. This allows to detect decay very early and to differentiate between decay of wood and decay of the modifying agent. The testing of modified wood fibres and particles can be done in suitable mesh bags within a period of eight weeks under conditions close to EN 113.

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ARTIFICIAL WEATHERING OF WOOD MODIFIED WITH THE CYCLIC N-METHYLOL COMPOUNDS

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Keywords: wood modification, DMDHEU, weathering, photodegradation, dimensional stabilization.

ABSTRACT

Scots pine wood (*Pinus sylvestris* L.) was modified with 1,3-dimethylol-4,5-dihydroxyethyleneurea (DMDHEU) to different weight percent gains (WPGs), and then exposed to artificial weathering. The results show, that DMDHEU treatment can restrict weight losses of wood during weathering, and that the treatment of wood with DMDHEU to high WPGs stabilised lignin to some extent. Scanning electron microscopy revealed that DMDHEU treatment was highly effective in preventing the degradation of the wood cell wall during weathering. Cells in modified wood retained their shape very well during weathering.

INTRODUCTION

Weathering of wood is a superficial phenomenon, but the degradation of wood by weathering brings about the surface crack, dissociation of wood molecules, discoloration, and microbial growth. Several studies have focused on improving the weathering resistance of wood through chemical modification. Rowell *et al.* (1981) and Feist and Rowell (1982) found that wood modified with butylenes, methyl isocyanate or butylene oxide to weight percent gains (WPGs) in excess of 25 % was eroded to the same extent as untreated controls during artificial accelerated weathering. Acetylation reportedly reduced the weight loss of veneers during weathering compared to untreated controls (Feist *et al.* 1991). At a WPG of 18 %, the erosion of the surface was reduced by 50 %, while the acetyl content in the topmost layer (0.5 mm) of wood was also reduced by 50 %. The protection, however, was restricted to cellulose (Feist *et al.* 1991), and lignin was hardly protected (Kalnins *et al.* 1984). Acetylated wood exposed to accelerated weathering developed less cracks than similarly exposed untreated controls, however, greying of the surface was not reduced (Plackett *et al.* 1992). Evans *et al.* (2000) reported that veneers acetylated to low WPGs (5 and 10 %) showed larger losses in weight and tensile strength during weathering than unmodified controls. This was explained through increased delignification and depolymerisation of cellulose of acetylated veneers, respectively. At higher WPG (20 %), weight losses and degradation of holocellulose in acetylated veneers were lower than in the control. Nevertheless, acetylation to high weight gains was unable to prevent the erosion of the lignin-rich middle lamella during natural weathering. In an early study, the wood modified with DMDHEU has shown considerable dimensional stability and fungal resistance (Militz, 1993).

Sugi veneers modified with DMDHEU showed better surface performance (cracking and hangnail rating) and lower weight losses during natural and artificial weathering than untreated specimens (Sudiyanni *et al.* 1996). The two N-methylol groups in DMDHEU are able to react with hydroxyl groups of the cell wall polymers. A possible reaction with phenolic groups in lignin might reduce its photodegradation, because it increases the redox potential of these sites. In addition, DMDHEU might undergo self condensation resulting in the formation of a three-dimensional polymer matrix. This could act as a reinforcing agent for the cell wall matrix to replace lignin that is degraded during weathering. The aims of this study are to determine the effect DMDHEU treatment on the resistance of artificial and natural weathering.

EXPERIMENTAL

Wood modification

Wood veneers measuring 100 mm x 20 mm x 60 μ m (ltxr) were cut from the sound sapwood of Scots pine (*Pinus sylvestris L.*) boards. These veneers were modified with 1,3-dimethylol-4,5-dihydroxyethyleneurea (DMDHEU) to 10-48 % weight percent gains (WPGs). Then the veneers were exposed to artificial weathering in QUV for 144 hours together with the untreated controls.

Analysis methods

The weights of weathered veneers were determined during exposure to QUV. The mass losses were calculated according to the weight changes. FTIR spectra of weathered veneers and controls were obtained by a spectrophotometer with ATR technique. Treated veneers and controls (unweathered and weathered) were examined using a field-emission scanning electron microscope operating at an accelerating voltage of 5 kV.

RESULTS AND DISCUSSION

Changes in weight and composition of veneers

Overall during 144 hour artificial weathering, the weight losses of the untreated and modified veneers were similar. During the first 48 hours of exposure, however, the untreated veneers lost weight more rapidly than the modified specimens.

FT-IR analyses of veneers

Infrared spectra of DMDHEU-treated and unmodified veneers showed an absorption at 1505 cm⁻¹ (aromatic stretch of lignin) was absent from unmodified veneers after 72 hours exposure (Figure 1). Those bands assigned to cellulosic constituents did not change significantly as a result of weathering. Compared to unmodified veneers, spectra of treated veneers after weathering suggest that DMDHEU treatment at low WPG (10% and 25%) did not protect lignin from photodegradation. In veneers treated to 48 % WPG, however, the peak was retained for longer suggesting that at high WPG (> 25 %) DMDHEU partially photostabilises lignin.

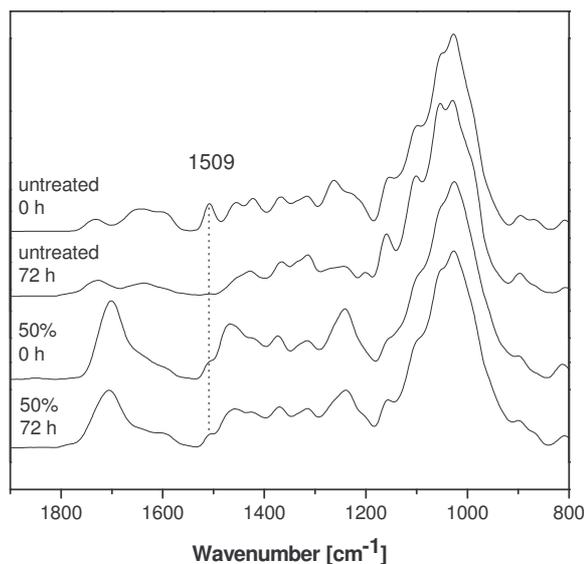


Figure 1: FT-IR spectra of weathered veneers after different exposure times

Electron microscopy of veneers

During weathering of untreated veneers, pronounced deformation of cell walls occurred within 48 hours (not shown). After 144 hours of weathering, tracheid walls were considerably thinner. The radial cell walls of tracheids in specimens treated with 10 % DMDHEU became thinner after 48 hours weathering, but the cells retained their shape. After 144 hours of weathering however the cell walls became wavy in appearance and cells lost their shape, but they were less distorted than cells in similarly exposed unmodified veneers. Treatment of veneers with 50 % DMDHEU further increased the resistance of tracheids to degradation during weathering. Even after 144 hours of weathering, the cell walls retained their initial shape and did not show the wavy appearance of exposed untreated veneers and those treated to low WPG exposed to weathering (Figure 2). Nevertheless, the cell wall thickness of veneers treated with 50 % DMDHEU was clearly reduced by weathering.

CONCLUSIONS

Treatment of Scots pine veneers with DMDHEU to low DMDHEU contents (9 % and 21 %) did not protect lignin in wood from photodegradation, but there was evidence from FTIR and weight loss measurements of weathered veneers that at higher DMDHEU content (32 %) the treatment stabilised lignin to a limited degree. The most noteworthy finding was the ability of DMDHEU to protect wood cell walls from degradation during weathering. This stabilizing effect of DMDHEU on the structure of wood in combination with its known ability to dimensionally stabilize wood suggests that DMDHEU may be a useful component of a treatment designed to protect wood from weathering and improve the performance of clear finishes on wood.

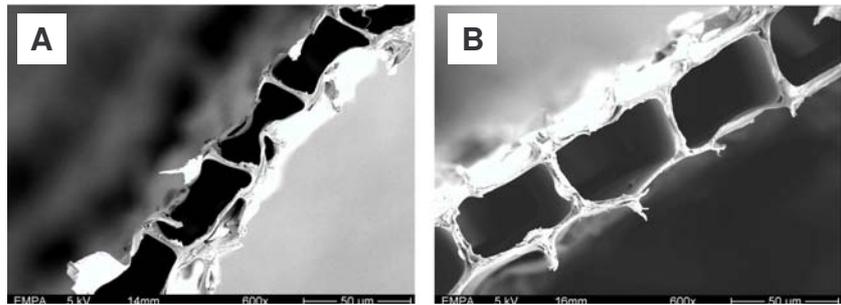


Figure 2. The microscopic cross sections of veneers weathered for 144 hours: A, untreated; B, 50% DMDHEU treated.

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EXPERIMENTAL STUDY OF THE EFFECT OF A LASER BEAM ON THE MORPHOLOGY OF WOOD SURFACES

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Keywords: Wood, cellulose, lignin, laser, melting, infrared, ultraviolet

ABSTRACT

The study reports on fundamental aspects of modification of wood by using a laser beam and relates different parameters such as wavelength λ , pulse duration τ_p , repetition rate F , and intensity E and focus to the surface morphology that presents melting processes that can be seen from microscopic observations (SEM). The penetration of water into laser treated surfaces is considerably suppressed. It is thought that the modification of wooden surfaces by laser beam represents a fundamental technology with many potential applications.

INTRODUCTION

Wood is a porous material whose porosity amounts from 60 % to 70 % for coniferous wood. The physical characteristics of wood, especially its moisture behaviour, strongly depend on the anatomical aspects. It consists of different chemical compounds among which cellulose, hemicellulose, and lignin are the most important ones. These chemical compounds consist of polymer chains that do not show a precise melting point but a glass transition temperature. Its value is distinct for lignin and cellulose and varies between 140°C and 200°C respectively (Sandermann and Augustin 1963). Therefore, "melting" of wood without burning or blackening of the surface cannot be achieved with conventional heat sources.

Orech (1975) measured the absorption spectrum of wood. Because of the absorption minimum at 1000 nm the lowest absorption is expected for Nd:YAG-lasers. Contrary to this, an effective absorption can be predicted for the UV- and IR-spectral range considering absorption of more than 80 % in this spectral range. Seltman (1995) was the first who published results of ablation experiments on wood surfaces by excimer lasers. The surface structure obtained by ablation was similar to that of a microtome cut for SEM investigation. Investigations by Henneberg (1997) and Panzner (1998) have shown that the ablation depth strongly depends on the local structure and the porosity of the wood.

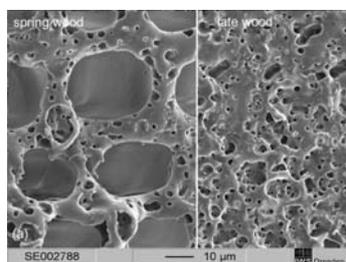
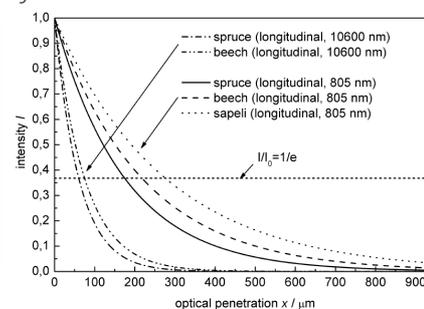
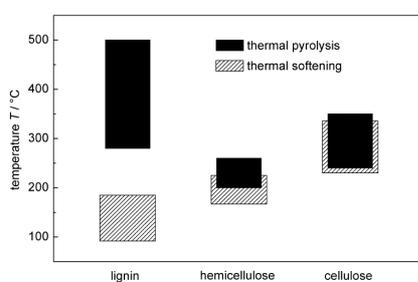
Carbonised or melted wood surface areas are well known but undesirable results of laser treatment of wood. They are usually removed. Thermal degradation is poorly controllable and unavoidable and as a result, the quality of machined wood will be reduced (Parameswaran 1982). High temperature during the cutting process (about 700°C, Arai *et al.* 1979) results in conversion of the cellular structure to glassy solid substance. Back had calculated the melting temperature for cellulose as about 450°C. Melting without combustion and carbonising should be possible if heating and cooling of the treated area are occurring in a very short time (Back 1973).

EXPERIMENTAL

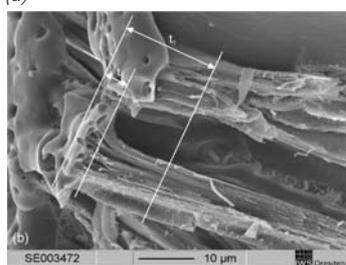
A CO₂-laser ($\lambda = 10.6 \mu\text{m}$) with 2.5 kW and pulse duration from 1 ms up to continuous mode was used because of the good absorption of wood in the range of 10 μm and the possible wide range of pulse duration. The laser beam was focused by a 45° focusing mirror of molybdenum coated copper with a focal length of 400 mm. To change the power density the average power of the laser were varied. Wood surfaces oriented according to the principal cut orientations have been investigated. Small samples (20 x 20 x 20 mm³) of beech, spruce and sapeli with sawn surfaces were used.

RESULTS AND DISCUSSION

Critical temperatures can be seen from Figure 1 which shows the temperature of phase transitions such as melting and of pyrolysis for the main constituents of wood: cellulose, hemicellulose, lignin. The viscosity of lignin becomes apparent at about 100°C. The pyrolysis temperature is lowest for hemicellulose: about 200°C. For lignin, pyrolysis occurs at much higher temperature than softening, whereas for cellulose the two processes nearly coincide.



(a)



(b)

Figure 3: SEM-image of spruce after laser irradiation with CO₂-laser, $\tau_p = 1 \text{ ms}$. (a) top view of cross cut, (b) cross-section, depth of molten layer $t_5 = 3.6 \mu\text{m}$, depth of thermal modification $t_7 = 15 \mu\text{m}$

Figure 1: Thermal softening and pyrolysis temperature of wood constituents (Wust 1998)

Figure 2: Optical penetration depth for spruce, beech and sapeli and selected wavelength of laser

Absorption of the laser irradiation is a necessary condition for modification of wood by laser (Figure 2). Experimental results of absorption measurement have shown smallest optical penetration depth for spruce at wavelengths 805 nm and 10.6 μm . The highest optical penetration depth was measured for sapeli. Additional optical reflection measurements have shown for all wood species a reflection by 90 % at 805 nm and a significant smaller reflection by less than 10 % at 10.6 μm . This means for irradiation a effective absorption of CO₂-laser at the surface and a possibly deeper penetration of Nd:YAG-laser combined with an evenly distributed heating effect. With CO₂-laser and pulse width in the range of 1 ms, the melting of wood surfaces without carbonising is observed (Figure 3a). The depth of the molten layer was measured using light and electron microscopy. It was found to be in the range from 2 μm up to 7 μm . Therefore the depth of thermal/ structural modifications was measured in the range from 5 μm up to 15 μm (Figure 3b).

Changes in physical properties, *i.e.* moisture absorption of the surface are realised measuring the wetting behaviour. For measurements, we have used a standard device for measuring the dynamic contact angle with distilled water. Measurements have shown for all wood species

after laser irradiation a contact angle of 80° (Figure 4). This means for spruce an increase by 130 % and for beech by 60 %. Comparing these results with microscopic observations, the change in wetting behaviour is assigned only to the molten edges on cut cells and not to the sealing of the surface.

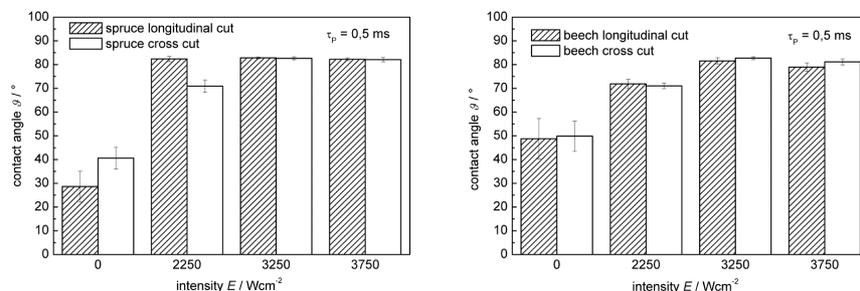


Figure 4: Contact angle of spruce and beech before and after laser irradiation with CO₂-laser

CONCLUSIONS

The study reports on fundamental aspects of these phenomena and relates different parameters such as wavelength, power density, pulse duration and focus to the surface morphology that presents melting processes that can be seen from microscopic observations.

The absorption of the laser beam varies with the changing wood structure during irradiation. The chemical composition, particularly the distribution of cellulose, hemicelluloses and lignin in the cell wall, leads to the observed changes of the threshold values for intensity and interaction time.

A field of irradiation parameters has been determined which guarantees melting of wood without pyrolysis. The surface temperature is assumed to be not higher than 200°C because above this temperature, according to the known thermal behaviour of the wood components, carbonising of hemicellulose and lignin is expected.

It has been found that irradiation with Nd:YAG-laser ($1,064\ \mu\text{m}$) requires an 8 to 1000 times higher beam intensity than irradiation with CO₂-laser ($10.6\ \mu\text{m}$), depending on irradiation time, to obtain about the same effect.

Both wetting behaviour and water absorption of all wood species tested here were changed by laser irradiation. The largest effect of laser irradiation was observed with spruce whereas only slight changes were obtained with sapeli.

Until recently laser application in wood technology has been restricted to a few techniques of cutting, perforating and engraving of wood and wood products. In view of this state of art it is highly justified to apply contemporary methods of material science to wood for better understanding of its structure and diverse properties in order to modify them with the aim of extended use.

ACKNOWLEDGEMENTS

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SURFACE PROPERTIES OF THERMALLY TREATED WOOD – WEAR, ABRASION AND HARDNESS

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Keywords: Abrasion resistance, hardness, shaker method, taber abraser, testing, thermal modification, wear resistance

ABSTRACT

The surface performance of thermally treated wood is characterised by its optical appearance, as well as by some mechanical properties including hardness, wear resistance, and abrasion resistance. In this study ‘mechanical’ surface properties, which are especially important for outdoor applications (terrace floorings, deckings), were investigated on heat treated timbers. The results from three different methods, *i.e.* the “shaker method”, the taber abraser method, and a Brinell hardness test were compared among each other and evaluated regarding their relevance for practice. Correlations were determined between the heat treatment intensity and the different surface properties. The influence of a thermal treatment on the surface performance of the timber is discussed, as well as the suitability of the different methods for testing of thermally modified wood.

INTRODUCTION

Relevance of surface properties in practice

Besides claddings and facades, thermally treated wood is mostly used as horticultural products, *e.g.* wooden decks, floorings, steps and stairs. Concerning these applications, two types of hardness properties of modified wood are differentiable. ‘Mechanical hardness’, which is the load carrying capacity of the material, is the critical property for all load bearing applications. On the other hand ‘surface hardness’ in terms of resistance to abrasion, splintering and flake offs is of higher importance for all non- or less-load-bearing applications. Especially for floorings and deckings this ‘surface hardness’ becomes the decisive property of the material. Although hardness is the most often reported surface property of heat treated wood (*i.a.* Jämsä and Viitaniemi 2001), it is well known, that thermally treated wood becomes more brittle and tends to show more splinters and flake offs compared to untreated wood (Jämsä and Viitaniemi 2001, Militz 2000, Rapp and Sailer 2001), whereby this becomes at least as critical as hardness for heat treated materials. Therefore, in this study two different abrasion tests and a standard Brinell hardness test were carried out by using wood heat treated with certain intensities to compare the results among each other.

Abrasion resistance - Suitable test methods

Abrasion is described as a combination of different stress types, like shearing-, compressive-, impact-, and friction-stresses, which all occur together on the wood surface and show an increased effect by the impact of sand or other particles (Kollmann 1981). Only a few tools for

the determination of this measurands can be found in literature and standards, which are mainly blasting techniques or sanding machines, as the Taber abraser, one of the few standardised methods.

The Taber abraser method according to DIN EN 438-2 (1992) was developed for testing High Pressure Laminated (HPL) boards. A rotating sand paper is pressed on the board with a defined force and the number of rounds, which is needed for the abrasion of the top layer is measured. It is obvious, that the principle of this testing method is not suitable for testing of thermally treated solid wood and has to be modified, even if it is possible to get board-like specimens of at least 100 x 100 mm².

Against the background of the shown disadvantages, a new method was developed with special focus on testing of thermally modified wood. Therefore, a test device was chosen, which consists of an ordinary laboratory overhead shaker fitted with polyethylene flasks. The flasks were filled with small solid wood specimens and an abrasive. This way solid wood specimens were abraded in their total volume by shaking them, wherefore the method was henceforth called the 'shaker method', described for the first time by Brischke and Rapp (2004).

EXPERIMENTAL

Material and heat treatments

For all three experiments, wood heat treated up to certain decrease in mass and axially matched untreated controls were used. For the Taber abraser tests and the Brinell hardness tests, beech (*Fagus sylvatica* L.) and silver fir (*Abies alba* Mill.) were used. Specimens of 120 x 120 x 16 mm³ were wrapped in aluminum foil and heat treated in an air atmosphere. For the 'Shaker' tests, oak (*Quercus petraea* Liebl.) and Scots pine (*Pinus sylvestris* L.) were added and specimens of 35 x 10 x 10 mm³ were heat treated as described for the other tests. The decrease in mass by the heat treatment was determined for all specimens by weighing them before and after the treatment.

Resistance to abrasion – Taber abraser method

The Taber abraser tests were carried out according to EN 438-2 (1992). The following modifications were made in order to allow testing of solid wood: A total of 27 specimens of 100 x 100 x 7 mm³ were cut out of the heat treated samples and conditioned in 20°C/65% RH. The tree rings of all specimens were oriented 45° to their cutting edges. After weighing and measuring of the thickness at 4 points, the specimens were clamped into the Taber abraser and abraded with sanding paper S-42 with approx. 60 min⁻¹ for 1000 rounds. Afterwards the mass loss and the decrease in thickness by abrasion were determined.

Resistance to abrasion – Shaker method

After Brischke and Rapp (2004) the resistance to abrasion was determined as follows: For each wood species a total of 120 heat treated specimens and 30 untreated controls was tested. Therefore the specimens of 35 x 10 x 10 mm³ were oven dried and weighed. Five of them were put into a polyethylene flask of 0.5 l together with 400 g of steel balls of 6 mm diameter. The filled flasks were put in an overhead shaker and rotated at 28 min⁻¹ for 72 hours. After this, the specimens were cleansed of wood dust by air pressure, oven dried and weighed

again to determine the abrasion in terms of mass loss. Five specimens were weighed together to give one replicate.

Brinell hardness

The Brinell hardness was determined according to DIN EN 1534 (2000) with a hardness testing machine (Zwick and Co., Einsingen) with the same specimens, which were used for the Taber abraser tests. At 5 measuring points a steel ball (10mm diameter) was pressed into the wood with 500 N for 25 s and the imprints of the calottes were measured. For each specimen the 5 single values were averaged for calculation of the Brinell hardness.

RESULTS AND DISCUSSION

The results from the Taber abraser tests (Figure 5) showed a correlation between the loss in mass, and thickness respectively, and the heat treatment intensity in terms of decrease in mass by the treatment. Even if a strong correlation was not found, the influence of the thermal modification on the resistance to abrasion became evident. The pure grinding by the Taber abraser seemed not to be a very critical stress type for heat treated wood, because neither the beech wood nor the silver fir samples showed an abrasion higher than 1 % decrease in thickness even for the highest treatment intensities.

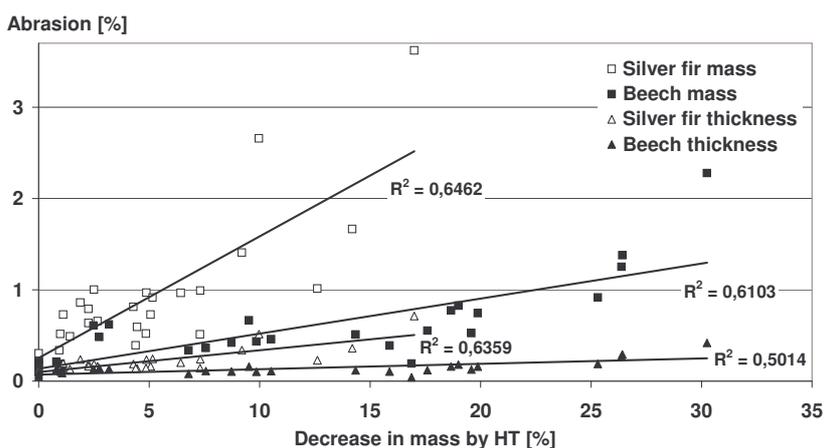


Figure 5: Correlation between the abrasion determined with a Taber abraser and the intensity of heat treatments expressed by the decrease in mass determined for silver fir and beech samples

As can be seen from Figure 2 both hardwoods (oak and beech) were only very slightly influenced by the heat treatment in terms of their resistance to abrasion when applying the Shaker method. Absolutely in contrast, a mass loss by abrasion up to 6 % for pine and up to 14 % for silver fir was found. Compared to the abrasion of beech, a factor of 12 was calculated. These results showed that the 'surface hardness' (mentioned at the beginning) is at least of the same importance as the 'mechanical hardness', which is already well known for thermally treated wood (Bengtsson *et al.* 2002, Brischke and Rapp 2004, Kamdem *et al.* 2002, Rapp and Sailer 2001, Seborg *et al.* 1953, Syrjänen and Kangas 2000, Viitanen *et al.* 1994). When comparing the typical damage caused by the Taber abraser and by the Shaker method (Mass loss after fungal attack by *Poria placenta*) with examples of worn wood in service, it becomes obvious, that a more realistic abrasion stress is induced by the

Shaker method, *e.g.* broken and rounded edges of the specimens, or a decking board respectively.

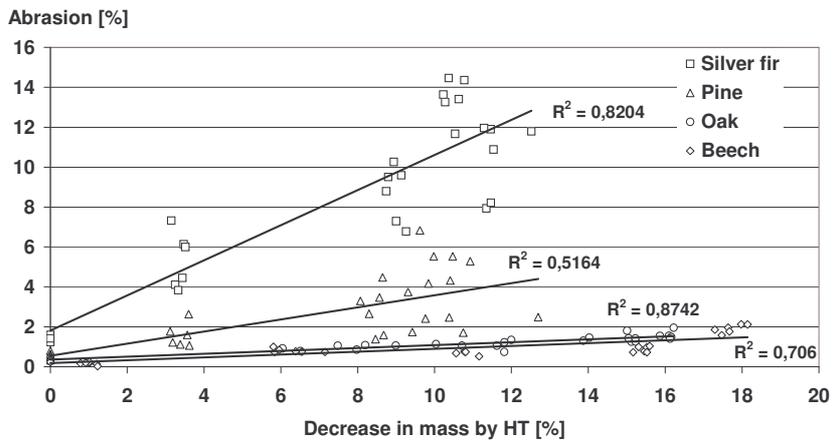


Figure 6: Correlation between the abrasion by shaking steel balls and the intensity of heat treatments expressed by the decrease in mass determined for silver fir, pine, oak and beech samples

The decrease in Brinell hardness correlated well with increasing intensity of the heat treatment, but was found to be less critical than the decrease in abrasion resistance determined in the Shaker test.



Figure 7: Abrased specimens: left: surface of a heat treated beech specimen after 1000 rounds in the Taber abraser (x10); right: heat treated silver fir specimens after 72 h abrasion in the shaker

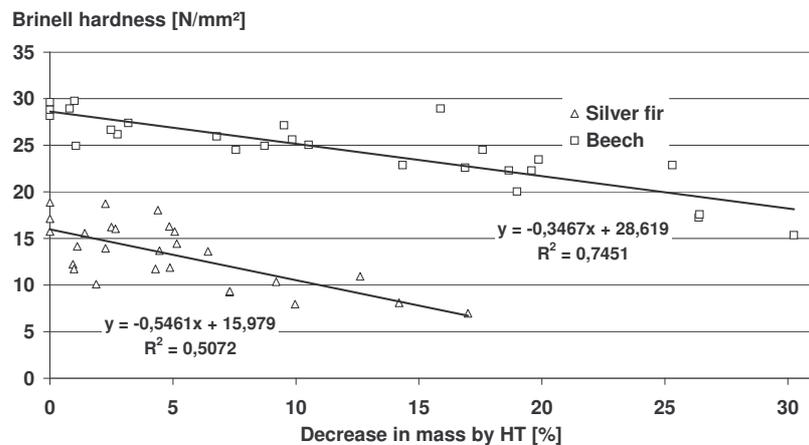


Figure 8: Correlation between the Brinell hardness and the intensity of heat treatments expressed by the decrease in mass determined for silver fir and beech wood

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DETECTION OF DECAY IN MODIFIED WOOD USING ULTRASOUND

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Key words: Decay evaluation, dynamic modules of elasticity, modified wood, Round Robin, soil bed testing, ultrasonic pulse

ABSTRACT

In this study, modified wood samples were tested according to the extended standardised test procedures of ENV 807 (3 types of soils). A Round Robin test was carried out at two laboratories: Swedish National Testing and Research Institute and Norwegian Forest Research Institute. The different soil types used were conifer forest soil (pH 4.6), soil from the Simlångsdalen test field (pH 5.2) and garden compost soil (pH 7.4). The wood modifications used were furfurylation (Visorwood), acetylation and heat treatment (Thermowood). Other materials tested were linseed oil impregnated pine, reference preservative (CC and CCA) treated pine and *Robinia psuedoaccacia* heartwood. A dynamic MOE (MOE_{dyn}) test device based on measurement of ultrasonic pulse propagation was used for non-destructive decay strength evaluation during the incubation period. The MOE values were correlated to measured decay mass loss of the test specimens after different periods of exposure to the soils. Type of fungal attack was also evaluated using light microscopy. Results from preliminary studies indicate that ultrasound seems to be an excellent tool for evaluation of early brown rot decay. It also seems to be feasible for detecting white rot. However it does not seem to be very accurate in evaluating early stages of soft rot decay.

INTRODUCTION

Reliable, reproducible and fast methods for evaluation of new wood modifications and wood preservatives are important. Several European standards are available to test and evaluate durability of these wood materials in field and laboratory. However, the evaluation criteria are not sensitive enough to detect early decay. Furthermore, some of the evaluation methods are subjective and destructive. There is therefore a need for additional fast and objective evaluation methods.

Mass loss calculation (after weighting the samples in oven-dry condition) and probing with a sharp or blunt tool (e.g. knife) can be regarded as destructive evaluation methods. They are not very sensitive tools to detect early stages of decay. Strength testing provides quantitative and objective results and has been shown to be a reliable alternative test for evaluation of fungal attack of timber (Hardie 1980, Gray 1986).

Both static and dynamic methods can be used for MOE measurement. The traditional method is static bending described in standards for MOE determination like EN 408 (1995) and Kucera (1992). One disadvantage is that the static method can be regarded as semi-destructive. In already decayed samples the bars of the testing equipment will irreversibly

damage the samples. Dynamic methods are either based on resonance vibration excitation (eigen-frequency) or ultrasonic pulse excitation (Gray 1986, Görlacher 1984). Dynamic methods are less frequently used than static, but have some advantages compared to the static method. The non-destructive nature of dynamic methods is of particular interest for evaluation of wood decay. They also give the opportunity for on-site measurements and reductions in testing time and labour costs (Machek *et al.* 2001). A high correlation between dynamic MOE and static MOE has been reported (*e.g.* Pellerin 1965, Gerhards 1975, Görlacher 1984, Blass and Gard 1994, Perstorper 1994, Machek *et al.* 1998 & 2001, Grinda and Göller 2005 b). From literature it is known that dynamic test methods tend to give higher MOE values than static methods (Kollmann 1968). Some studies have been published about the applicability of the vibration method in the assessment of wood decay (Machek *et al.* 1997, Machek *et al.* 1998, 2001). Machek *et al.* (1998, 2001) found that static MOE and dynamic MOE losses determined for decayed wood specimens followed the same trend as the mass loss. However, MOE determination provided a much higher sensitivity compared to mass losses.

In some sawmills, ultrasonic methods are used for evaluation of quality and strength. No study has been published on the assessment of the ultrasonic MOE method applied for laboratory decay test evaluation.

EXPERIMENTAL

The wood modifications used were: Visorwood 25 WPG, 37 WPG and 50 WPG, Thermowood D 212°C, Thermowood Spruce D 212°C and Acetylated 23 WPG and 30 WPG. The reference treatments were with CC preservative (Kemwood KC73 at 0.33 %, 0.67 % and 1.33 % concentration, were the highest gives the retention level for NWPC Class A), CCA-preservative (CT 106 at 0.6 % and 1,3 % conc, corresponding to NWPC Class AB and Class A retention level), and Linseed oil impregnation. Heartwood of *Robinia pseudoaccacia* was included as an additional reference and untreated Scots pine sapwood as control. Scots pine sapwood (*Pinus sylvestris* L.) was used for all the different modifications and preservative treatments except for the Thermowood spruce. The samples had the ENV 807 dimensions, 5 x 10 x 100 mm³. The treated samples were leached according to EN 84 before decay testing. The decay test used was Terrestrial MicroCosm (TMC) test (Edlund 1998), a modified ENV 807 (2001). Three different types of soil were used: mixed soil from coniferous forest (50/50 from test fields in Ås, Norway and Ingvallsbenning, Sweden, respectively), garden compost from Sweden and soil from the Swedish test field in Simlångsdalen (Table 1).

Table 1: Soil characteristics of the three test soils; moisture at water holding capacity and pH.

	Conifer forest	Garden compost	Simlångsdalen test field
pH	4.6	7.4	5.2
Moisture content at WHC % (m/m)	137.5	101.7	19.7

Dynamic MOE measurements (MOE_{dyn}) were performed directly after leaching, at wood moisture contents above fibre saturation. The samples were conditioned before decay testing. During decay testing the samples are tested every 8 week using MOE_{dyn} above the fibre

saturation point. These preliminary data give the results after 8 and 16 weeks.

The MOE test device was Pundit Plus –ultrasound (CNS Farnell, UK). An ultra/phonic conductivity gel (Pharmaceutical Innovations Inc.) was applied on the end-grain of the wood specimens to improve the contact between the transducers (200 kHz) and the wood sample. The transit time was measured. To calculate MOE, Equation 1 was used:

$$MOE_{dyn} = \left(\frac{l}{t}\right)^2 \cdot \frac{m}{v} \quad (1)$$

Where: l = length, t = transit time, m = mass, and v = volume

RESULTS AND DISCUSSION

Results from preliminary studies show that ultrasound is a good tool for evaluation of early decay of brown rot. It also seems feasible for detecting white rot. However it seems so far not very accurate in evaluating early stages of soft rot decay. The differences detected by ultrasonic dynamic MOE between the different decay types are probably due to the nature of their decay. Brown rot fungi are known to cause more rapid strength loss at lower mass losses than white rot fungi. Soft rot causes surface softening and since the ultrasound measures transit time in the longitudinal direction, soft rot does not influence the ultrasound to the same extent as brown rot.

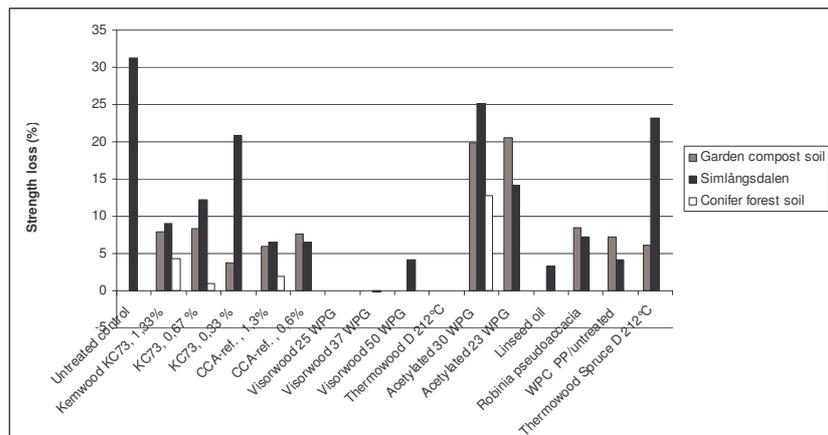


Figure 1: Strength loss (mean values) in test samples after 8 weeks given as percent of initial strength. The results include the incorrect values for acetylated wood (see discussion below).

From static measurements it is known that mechanical properties of wood decrease with increasing moisture content (Kollmann and Coté 1968, Skaar 1988). Below the fibre saturation point (FSP) water is found in the cell wall, while above FSP water is found both bound and as free water in the lumen. Using ultrasound below FSP, the water molecules move in phase with the vibrating wood cell wall. The binding strength of free water with the cell wall above FSP is relatively low (Wang *et al.* 2002). Therefore, it will not oscillate simultaneously with the cell wall material at a high frequency vibration. Therefore vibration loss increases rapidly when wood moisture content is above the FSP. An increase in moisture will therefore cause a decrease in the velocity of ultrasonic pulses. This can be solved by quantifying the free water

according to Sobue (1993). Testing above FSP is supported by other studies. Wang and Chuang (2000) found that the moisture content below the fibre saturation point had a larger effect on ultrasonic velocity than that above the fibre saturation point.

The soil from Simlångsdalen seems so far to be the most active soil followed by the garden compost soil. The soil from the coniferous forest was not unexpectedly the least active soil in this test.

The preliminary results from this study of the decrease of MOE are presented as the relative decrease compared to the initial strength. Therefore a k-value according to Sobue (1993) should not be needed as long as the moisture was the same. However, we found that for some of the treatments the FSP was dramatically shifted and the time to condition the samples to FSP was not enough to reach FSP. This is clearly visible for the acetylated wood, which gave a false decrease in MOE (the higher the acetylation level the larger the decrease). In fact, there was no trace of decay in the acetylated specimens and no mass loss at all. Therefore, the sorption abilities of the modified wood samples need to be tested. An exact "k"-value for all modifications based on this data also needs to be calculated.

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CHAPTER 7

MARKET POTENTIAL

CONTROL SYSTEMS, QUALITY ASSESSMENT AND CERTIFICATION OF MODIFIED WOOD FOR MARKET INTRODUCTION

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Keywords: Quality assessment, control systems, modified wood

ABSTRACT

The existing Dutch national assessment directive for product certification of timber modification will be explained. This includes a comprehensive description of the outlined procedures and requirements. Aspects for the requirements for: the production process, the product, regarding the quality system of the applicant and regarding the marking, identification and trace-ability will be touched upon. Attention is given to matters concerning the uniformity and measuring the reproduce-ability of the production process.

INTRODUCTION

Modified wood has now established its name. Thermal treatments have already been penetrating the market for a number of years and several chemical modification processes are just emerging. Since both traditional wood preservation and the use of tropical species are under political and consumer pressure, the timber industries are seeking alternatives. The use of home grown species with enhanced qualities could be the ultimate solution to this problem. However, the market and the end-users need some type of reliable system for quality and proper use in suitable applications. The market needs to be protected against inferiority and misleading claims of material performance. It is important to provide clarity where a modified material can be used and how it should be used. Many questions arise along with the introduction of new materials. What are the basic properties and what are the special properties? What are the difference performances of the material between the different treatments. On the Dutch market now, already more than ten brands of thermally treated wood can be distinguished and this process is continuing today. Although many aspects of modified wood have been researched on a laboratory scale and demonstration level, long-term experience with modified wood is rather limited. On the other hand, for this new emerging industry, also the image of modified wood should not be damaged by inappropriate use of the material. From both sides, producers and end-users, the urge for a comprehensive and collectively accepted quality control system is becoming stronger.

For the European market, it is important that a comprehensive quality control system is commonly accepted and internationally recognised. In different countries initiatives have been made to produce guidelines, quality control systems and national assessment directives. In The Netherlands, a 'National assessment directive for the ®Komo product certificate Timber modification' has been used for several years. In Finland, the association of Finnish heat treating companies has completed a handbook and is developing a quality control system. European-wide, a recent installed CEN committee

(CEN/TC 175/WG 3/TG6) is now preparing a working document for a European standard on thermally modified timber.

The aim of this paper is to emphasise the importance of a uniform quality control system for the market introduction of modified wood within Europe.

EXPERIMENTAL

The process of drawing up a national assessment directive, as is done in The Netherlands, is described below. A national assessment directive, as the here described directive on modified wood, can be drawn up when there is an apparent demand in the market for certification. For that purpose an advisory committee shall be installed consisting of a group composed as widely as possible of persons concerned with the subject. The draft of the directive drawn up by this advisory committee is presented to a committee of experts. After approval, this draft directive shall be published for comments and consequently be presented to and accepted by the Building Harmonisation Committee of the Building Quality Foundation.

Prior to the process the definition or criteria, of what is modified timber and what is timber modification, needed to be made. For modified timber the following definition was accepted: "timber that has endured a treatment during which the cell wall material has changed at molecular level, in such a way that, dependent on the modification technology applied, properties of the timber, such as durability and form stability, are improved". Timber modification is a collective term for technologies directed at the changing of physical and chemical properties of cell wall material in timber, different from technologies making use of biocides. The manner in which the cell wall material is modified, depends on the method applied. At the present state of the technology and knowledge, the methods can be subdivided into the following treatments:

- thermal,
- chemical
- biological
- enzymatic

RESULTS AND DISCUSSION

For modified timber, the process of drawing up a national assessment directive started in 1997. The directive was officially approved and effective in 2003. The main subjects on which this directive is built, are:

- Process requirements
- Product requirements
- Quality system
- Control by the certification body
- Requirements regarding the marking, identification and traceability

Process requirements

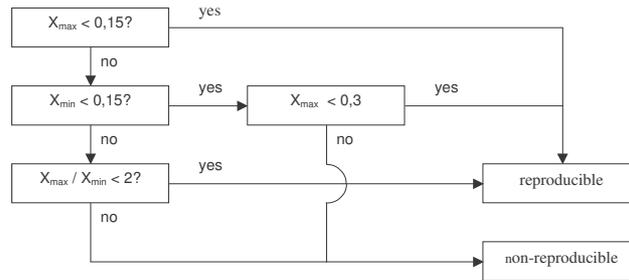
In general for the process requirements, the producing company shall dispose of production equipment, by which products can be manufactured having a constant quality. The producer shall formulate the requirements of the raw materials. Aspects of the raw materials, which affect the process parameters or the end product, have to be named. All relevant data regarding the production process shall be recorded in writing by means of an automatic registration. For matters of the trace-ability each run has to be given a unique number. The trace-ability has to be guaranteed by the numbering of bundles, until bundles or packing unit is disturbed during the use in the application.

Uniformity of the production process is important with respect to uniformity and a constant quality of the products. The producer makes sure that the uniformity of the production process is maintained, by showing that the process conditions are equal throughout the installation.

Reproduce-ability of the production process

For end-users of modified wood, it is important that the quality and material properties of the material are invariable in time. Products in which modified wood is a basic material, need to reach a specific quality level. Invariability of one of the delivered base materials disturbs the quality guarantee a product producer is giving on his product. For this purpose the producer should demonstrate that the process is reproducible. In order to do this, at least one timber species will be subjected to a durability test against attack by basidiomycetes and by soft rot causing fungi. The reproduce-ability will be evaluated on the bases of the results of the durability tests. In order to have a strong link between other properties of the treated wood, produced under the identical conditions, corresponding samples are taken for additional measurements. Apart from durability test, pieces shall be subjected to the determination of bending strength, Janka-hardness and modulus of elasticity, density and equilibrium moisture content and shrinkage behaviour. Sampling of the treated wood is important to gain a good overview of the reproduce-ability. In this framework, these samples should be manufactured from modified boards originating from at least 9 boards, which are evenly divided over three different treatment batches. Five recurrences are taken per board. This means that 45 samples per fungus are tested for the reproduce-ability test.

Attack by basidiomycetes is determined by the combination of pre-leaching according to NEN-EN 84 and laboratory fungi test according to NEN-EN 113. Attack by fungi causing soft rot will be determined by PR-ENV 807. Using the results of the mass losses in the durability tests, the so-called x-value is being calculated. This is done for each run and for each type of fungus, by dividing the average attack of the treated samples by the average attack of the reference samples (pine sapwood in the case of modified softwood and beech in the case of modified hardwood). The process can be considered reproducible when the results comply with the following criteria (see Fig. 1):



X = the median value of all x-values per batch.
 X_{max} = the x-value of the batch with the highest median value of all x-values
 X_{min} = the x-value of the batch with the lowest median value of all x-values

Figure 1: Flow diagram of reproduce-ability according NAD 0605: Timber modification.

The relevant durability tests will not be carried out, in case the durability of the modified timber in the various hazard classes, at the explicit request of the producer, shall not be included in the quality declaration as a (claimed) performance.

Product requirements

Depending on the application of the modified timber, selected product requirements must be determined. Together with the certifying body (in the Netherlands, SKH) and independently of the application of the modified timber, it will be determined which properties of the material shall be tested and documented. The product specifications will be included in the quality declaration (see Table1). The product specifications are stated as absolute or as relative values (*i.e.* in respect of the original material or wood species).

Table 1: Product properties selectively to be testes and documented for NAD 0605 Timber Modification

Product property:	Value:
Timber species	
Type of timber modification	
Durability class	
To be applied in hazard class(es)	
Density and spreading	
Equilibrium moisture content (at 65% RH and 20°C)	
Water absorption, speed	
Water absorption, extent of	
Shrinkage and swelling behaviour radially	
'Shrinkage and swelling behaviour tangentially	
Shrinkage and swelling behaviour radially	
Shrinkage and swelling behaviour tangentially	
Adhesives for non-load bearing applications	
Adhesives for load bearing applications	
Finish	
Colour value	
UV stability	
Bending strength	
Janka-hardness	
Modulus of elasticity	
Strength class	
Impact bending strength	
Processing	
Class of contribution to fire propagation	
Smoke density of the smoke production	
Emission of hazardous substances	

Of the above mentioned material properties can be divide into ten main product requirements which can be determined:

1. Durability
2. EMC / water absorption
3. Dimensional stability
4. Glue-ability
5. Suitability for finishing systems
6. Colour
7. Mechanical properties
8. Processing properties
9. Fire behaviour
10. Emission of harmful material

How extensive the property will be determined is also dependent on whether this property is put forward as a minor property or an essential property. For instance in the case of dimensional stability, this can be of minor interest when applying modified timber or could an essential aspect the aimed application. In the first instance, the dimensional change shall only be determined in a trajectory between two measurement points; from 'wet' (this is above the fibre saturation point obtained by submerging) to an equilibrium situation at a relative humidity (RH) of 65 %. In case that the dimensional stability is an essential property, a broad range with more measure points is needed to be determined. The following climates shall pass the following phases: oven dry, 25 % RH, 35 % RH, 50 % RH, 65 % RH, 80 % RH, 90 % RH and water saturated (in this and reversed sequence). From the swelling and shrinkage data the ASE (anti-shrink/swelling efficiency) can be calculated subsequently. For the determination of all the properties mentioned in Table 1 if possible European standards are applied. The complete list of documents and standards referred to for determination of properties in this directive is listed as an appendix to this paper.

Quality system

The quality system is divided into:

1. Internal quality management of the producer
2. External quality control

The internal quality management of the producer should cover the following issues:

- Responsibility of the producer
- Reporting changes
- Retention of the product properties
- Inspection and testing
- Handling of claims
- Internal quality control

The certification body, in accordance with the product certification regulations, does the external quality control. It controls during the pre-certification inspection whether the relevant factory complies with the drawn up requirements as given in this national directive. A report of the pre-certification inspection is made, on the basis of which the [®]KOMO product certificate shall be issued, with or without certain conditions.

Requirements regarding the marking, identification and trace-ability

The modified timber shall be marked per bundle or packing unit by applying the following issues:

- the certification logo (KOMO® logo);
- the product certificate number of the producer of the modified timber;
- the unique production/run number;
- listing the application for which the timber has been modified by means of a colour or letter code, based on the use classes in accordance with NEN-EN 335-1 (see table 2);
- listing the original timber species

The table with codes of the application for which the timber has been modified based on the hazard classes has been shown in Table 2.

Table 2: Target applications for the treated material in use classes and corresponding codes

Hazard class	Description	Colour	Letter code
1	Above ground, not exposed to the weather	black	L
2	Above ground, with risk of wetting	orange	L
3	Above ground and periodically in contact with rain water	blue	L
4	Soil contact and soil water contact	white	G
	Permanently in contact with freshwater	green	W
5	Permanently in contact with brackish or saline water	red	Z

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Appendix

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Building Act 2003 Stb. 2001, 410; Stb. 2002, 203, 516, 518, 582 and the Ministerial Regulation Stct. 2002, 241.

* In case a year has been placed after the number of a revised or supplementary standard, it refers to the year in which the latest publicised correction or supplement has been issued.

** Consult the 'Overview of quality declarations in the building industry' of SBK for the correct date of this BRL.

THE USE OF WOOD MODIFIED BY HEAT-TREATMENT FOR MUSICAL INSTRUMENTS

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Keywords: acoustic, heat-treatment, musical instruments, thermally modified timber

ABSTRACT

The Institute for Research and Development of Musical Instruments Zwota, adjacent institute of Dresden University of Technology, and the chair for Wood and Fibrous Materials Technology of Dresden University of Technology worked on a research project promoted by the Federal Ministry of Economics and Labour for the application of thermally modified wood in musical instruments. The goal of this project was to analyse the changed physical, anatomical and chemical characteristics of modified woods and to compare them to characteristics being relevant for musical instruments. Conclusions on the possible use of these woods in musical instruments were drawn. By a special treatment, the physical-technical characteristics of wood can be changed in such a way that they correspond to the requirements for use in musical instruments better than unmodified woods. Above all, this is reduced moisture sorption, better durability and higher dimensional stability, as well as acoustic characteristics, which can be compared with an 'artificial aging'. The thermal modification of wood results in an improvement of objectively measurable properties, which permits conclusions on improved sound characteristics. The potential use in musical instruments opens up a large new area for the application of thermally modified wood.

INTRODUCTION

The rising demands for quality by consumers and the large number of musical instruments on the world market increase the demands for constantly better quality products. It is also the case that in the next years on the international wood market there will be a reduction in the supply of specific woods. It is therefore necessary to investigate alternatives, in order to support musical instrument manufacturers with solutions to these problems. A working hypothesis formed the basis for the project:

One of the possibilities to supply the timber demand for the musical instrument industry could be the use of thermally modified wood.

With this method physical and technical characteristics of the wood are to be changed in such a way that it can be used in musical instruments.

The following goals were to be realised by thermal modification:

- Use of woods, which were, so far, not used for musical instruments
- Replacement of expensive or rare imported timbers
- Improvement of the characteristics of wood for the use in musical instruments
- Improved of sorption behaviour: Decrease shrinking behaviour
- Artificial aging of the wood
- Decrease of long storage times

EXPERIMENTAL

In this project thermally modified wood made by different European manufacturers was analysed. Physical-technological, anatomical, chemical and acoustical characteristics were compared with the unmodified twin sample. Extensive investigations were carried out on wood supplied by Thermoholz Austria GmbH. This material was treated at three different levels (little, medium, strong). The unmodified twin-sample was retained and tested separately.

The test program covered mechanical examinations (determination of Young's modulus by dynamic and destructive methods, modal analysis, stress-strain behaviour, sound velocity, damping and impact bending strength), anatomical investigations in the scanning electron microscope, chemical analyses (hot water and chilled water extractions and saliva extractions, UV-VIS-analysis of the extracts and investigations in a GC-MS-System), analyses of water absorption, diffusion and dimensional stability as well as examinations on the workability, painting and gluing. The project ended with the production and examination of parts of musical instruments.

RESULTS AND DISCUSSION

In this publication it is just possible to deal with some special test results more exactly. The complete results are contained in the final reports of both research establishments (Wagenführ and Pfriem 2005, Eichelberger 2005).

Mechanical investigations

For the objective determination of sound characteristics of wood, the loss and radiative damping, as well as sound velocity and/or sound resistance are important characteristics. The sound propagation takes place (in first approximation) in the form of mechanical longitudinal waves (flexible wave, the particles of the medium swing in direction of propagation of the wave). The sound propagation depends on all parameters, which affect density, Youngs' modulus and shear modulus.

The determination of the Youngs' modulus was performed by non destructive testing methods using a dynamic measuring system and a measuring instrument working within the ultrasonic region (determination from the sound velocity and the density of the sample) and the determination by destructive examination in a three point bending test (Figure 1). The fracture behavior of thermally modified woods was analysed by strain-stress curves (Figure 2).

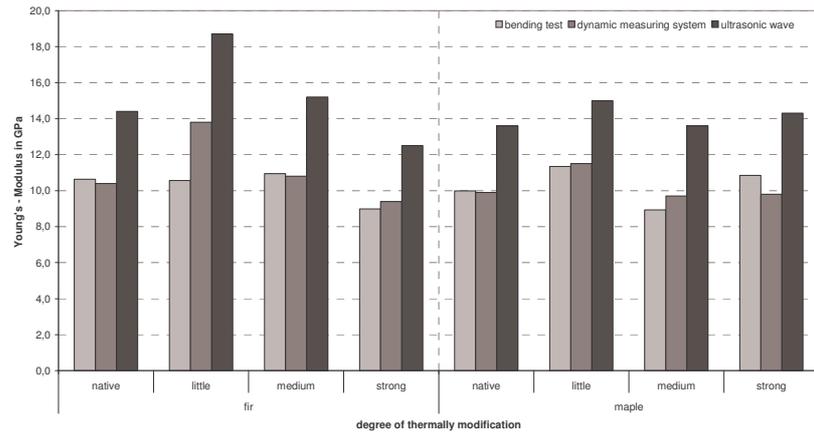


Figure 1: Young's modulus of fir and maple at different degrees of modification

The results of the three testing methods show that a relatively mild thermal modification tends to result in an increase of the Young's modulus and sound velocity but also to an embrittlement of the material. Earlier investigations of Schneider (1971) and Burmester (1973) are confirmed. A strong thermal modification leads to a degradation of the elastic and physical properties. This was also found by Sinn *et.al.* (2002). The increase of the Young's modulus and sound velocity by a relatively mild thermal modification is desired for the use in musical instruments (Schelleng 1963, Barlow 1997). In addition, a mass loss by thermal modification, which likewise positively affects the acoustic characteristics, takes place. Measurements using the ultrasonic wave result in higher characteristic values than measurements in the static or dynamic test, because the density is averaged over the cross section of the entire sample.

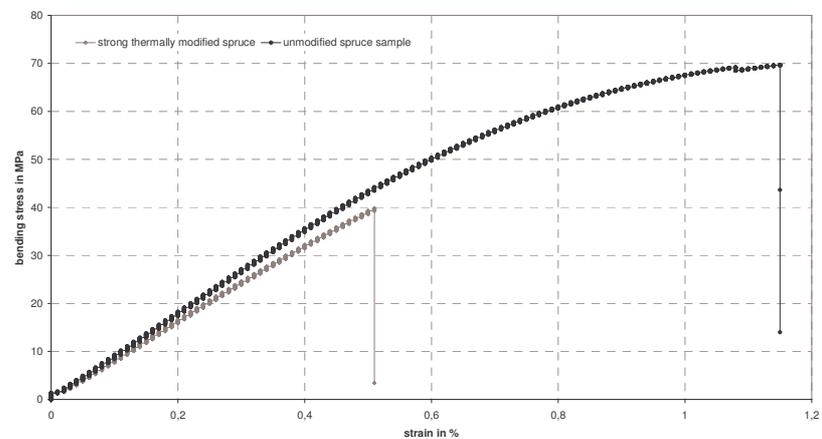


Figure 2: Strain-stress curves of thermally modified und unmodified spruce

With the bending test, the failure can already take place in the elastic range. That means that some strongly modified samples did not reach the proportional limit. This fact is shown by strain-stress curves in Figure 2. Thus, the reduction of the elongation at rupture in the longitudinal direction but above all, also the transverse direction is to be regarded as problematic by use of strongly modified woods.

Investigations to the dimensional stability during alternating climatic conditions

The improved dimensional stability of thermally modified woods was analysed by photogrammetric methods. The surfaces of the samples were determined three-dimensionally and afterwards the samples were subjected a cyclic alternating climatic conditions test. In Figures 3 and 4, the substantially larger dimension changes of the unmodified samples in comparison with the thermally modified twin sample is visible. The form of the unmodified sample is changed, in particular at the edges. The thermal modification leads to clearly reduced deformations of the wood in the climatic conditions test.

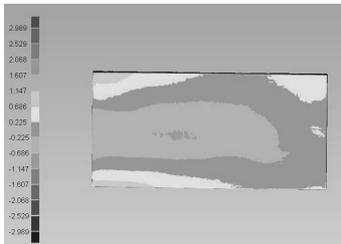


Figure 3: Dimension change of native maple after artificial weathering

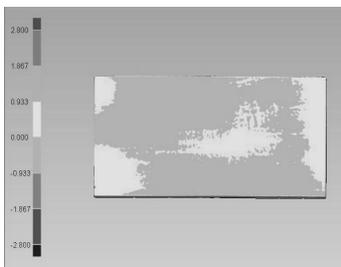


Figure 4: Dimension change of native maple after artificial weathering

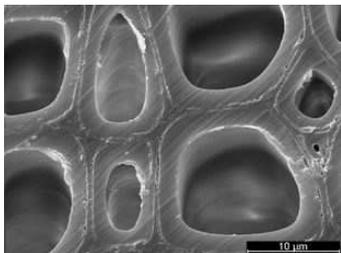


Figure 5: Scanning electron micrograph of native maple - transverse section

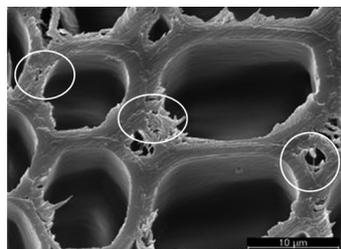


Figure 6: Scanning electron micrograph of thermally modified maple - transverse

Anatomical investigations

A longer continuous heat treatment (150° over 24 hours) leads to microcracks in the interfaces between the cell wall layers and within the central secondary layer. These cracks are led back as a result of stress phenomena after cell shrinking, because they proceed in particular from the corners of adjacent cells (Tjeerdsma *et al.* 1998). With hardwood, a loosening of the cell group between the S1 and S2-layer could be seen. A smoothing of the warty layer of beech wood as well as a change of the pit torus of spruce wood was found (Fengel 1966, Fengel and Wegener 1989).

Figure 5 and 6, clearly shows embrittlement of the sample after treatment, in particular from the border and in the S2-layer, which is recognisable by analysing strongly modified maple. The results confirm earlier investigations of Fengel 1966 and Tjeerdsma *et al.* 1998.

These defects can be the starting point of macroscopically noticeable damage. These defects could result in higher porosity of the wood, which was proven by other groups of researchers (Bächele *et al.* 2004, Junghans *et al.* 2005). This is to be due in particular to the degradation of hemicelluloses between the middle lamella and primary wall P and/or S1-layer (Tjeerdsma *et al.* 2002) and to the degradation of the cellulose chains (Kollmann *et al.* 1969). Such defects are marked in Figure 6.

Thus, the physically measurable changes of the strength and in particular the impact strength can be attributed to anatomical causes. Whole degradations of individual cell components cannot be observed. In fact, the anatomical cell structures are extensively unaltered.

A possible destruction of the pit membrane by a thermal treatment, as was described by some authors (Fengel 1966, Bächele *et al.* 2004), could not be proven by analysing scanning electron micrographs of radial cuts of strongly modified fir (Figures 7 and 8). In Figure 8 the break took place between the cell walls. The upper cell wall is removed to reveal the view of the bordered pit torus, which 'sticks' on the secondary wall of the cell which is under it.

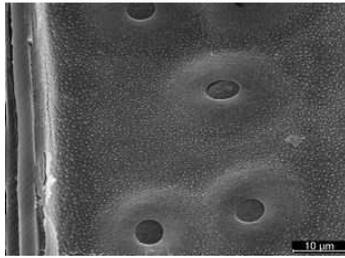


Figure 7: Scanning electron micrograph of native fir - radial section

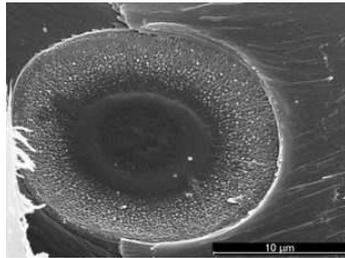


Figure 8 Scanning electron micrograph of strongly modified fir - radial section

Investigations to the workability in musical instruments

The investigations of the workability, painting and gluing properties demonstrates that the lacquer and glue systems usually used for the production of musical instruments can also be used for thermally modified wood. It was proven by optical edge angular measurement that the angle of edge of wetting is significantly increased from 30° to 42° by a relatively mild thermal modification. However the wood is still wetted sufficiently with these liquids. Due to these investigations, traditional production technologies of musical instrument making can be transferred for use of thermally modified wood in musical instruments.

Production and examination of musical instruments

Guitars were manufactured from relatively mild thermally modified spruce (Figure 9).



Figure 9: Guitar made of thermally modified spruce (right) und unmodified spruce (left)

Tests showed that guitars made from thermally modified woods exhibited just as good sounding and playing characteristics as guitars made from unmodified woods. This conclusion is confirmed by objective tests of the instruments. An evaluation of the instruments by their frequency characteristics was performed. The instrument being examined is excited at the bridge with a defined energy and the sound radiation resulting is measured (Ziegenhals 2000). Figure 10 shows the frequency characteristics of three guitars made with sound boards of thermally modified wood (F03303 to 05) compared with an identically constructed reference instrument (Reference line) made with an untreated spruce sound board.

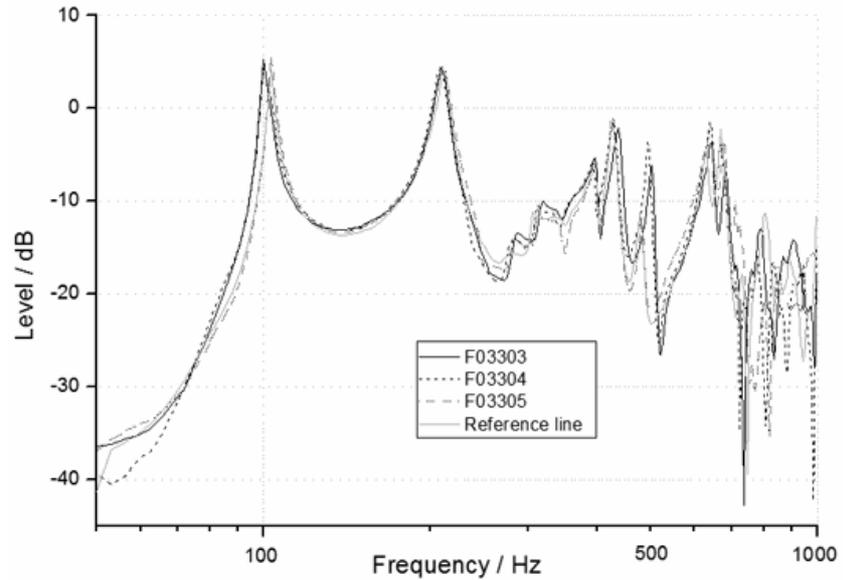


Figure 10: Comparison of the Frequency characteristics

Apart from a change of the acoustically relevant characteristics, thermally modified woods exhibit advantages concerning the dimensional stability and sorption in regard to alternating climatic conditions. With thermally modified woods, a material with favorable characteristics is available for musical instrument making. A pre-selection of the raw materials is however absolutely necessary. Inappropriate materials can hardly be improved. Earlier investigations of Gadd and D'Arcy (1986) could not be confirmed.

CONCLUSIONS

Due to these attainable changes of characteristic, the project assumed that for thermally modified woods three new application areas in so called small musical instruments were possible.

- Use in musical instruments, where high dimensional stability and low moisture sorption are required, for example in wind instruments, in addition, stringed and fretted instruments, which are played in different extreme climatic zones of the earth.
- Use in musical instruments, where specific sound characteristics are required, which otherwise can only be attained by the use of woods stored for a very long time, for example for stringed and fretted instruments. A reduction of storage times and in that way a significant saving on storage costs can be obtained.
- Since the thermally improved wood shows similar sound characteristics to naturally aged wood, it is suited for the restoration and reconstruction of old musical instruments.

The results obtained so far suggest that thermally modified wood for these ranges of application can represent a possible alternative. In the project thermally modified wood products of different European manufacturers were analysed under physical-technological, anatomical, chemical and sound and/or acoustic criteria and compared with the unmodified twin samples. Different wood species and different modification levels for the possible application fields were analysed. Parts of musical instruments were made of suitable thermally modified wood and tested regarding their acoustic and sound characteristics. A mild thermal treatment, leads to clear changes of the measurable acoustic characteristics, such as Young's modulus, damping and sound velocity. Past investigations into the workability, painting and gluing demonstrates that the lacquer and glue systems usually used for the production of musical instruments can be used for application of thermally modified wood. Due to these investigations, traditional production technologies of musical instrument making can be transferred for use of thermally modified wood in musical instruments. The use of these woods might create a problem in musical instruments played with a mouthpiece. At the present stage of research there is a slight possibility that saliva might extract more substances from the thermally modified wood, compared to unmodified wood. Due to the results accomplished so far, it is planned to expand the research on the use of thermally modified wood to larger instruments, like organs.

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HOW TO INTRODUCE ACETYLATED WOOD FROM THE FIRST COMMERCIAL PRODUCTION INTO EUROPE

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Keywords: Marketing, acetylation

ABSTRACT

This paper explains the introduction-strategy of acetylated wood into the market. The product is going to be produced commercially for the first time worldwide. The acetylated wood is "new" and is relatively new to many end users and therefore, it has to be carefully considered how to introduce this "new wood species". The information given will be about how the most value will be obtained from the product, which markets do you concentrate on, bulk or niche. Also how to identify synergy partners which will help to build on the acceptance in the market and help to build and expand the market. What strategy do you chose: differentiation, focus, customer intimacy, product leadership or combinations? How do you position the product in the market? What are the short-term strategies and what are the long-term strategies? This paper will give an explanation of the introduction of acetylated wood from the first commercial production worldwide.

INTRODUCTION

The world of the wood industry is changing rapidly. The supply is changing because the availability of quality tropical timbers is reducing. This due to harvesting methods used in the past, while the demand in countries like China is growing very fast. Besides this, more forests become protected by sustainable forest management labels to make certain there is forestry possible in the future. More attention is given to illegal harvesting of trees and actions are taken to reduce the illegal harvest as much as possible.

This all together makes the supply of quality tropical timbers become more difficult with the result that prices increase and often qualities fluctuate and finally reduce.

On the wood preservative side also many changes are going on. The use of preservative chemicals is becoming restricted in applications where people will be in contact with the treated wood. During the last few years some preservatives have been prohibited for use in large parts of the world. The list of prohibited chemicals is expected to grow in the near future in more countries.

In some applications, the market share of wood has decreased significantly. For example, the window industry has seen a significant reduction in the share of wood used. Plastic and aluminium have taken over the market share. The same goes for decking and cladding, where wood being replaced by composite materials.

Wood modification can be compared to the airplane industry. Until the 1930's, the airplane industry did not make a lot of progress in developing and improving the performances and uses of the airplanes. In the 1930's the Second World War was expected and the value of airplanes was recognised. From the mid 1930's until 1945 the development of airplanes was done at a very high speed. In 1945, aircraft with jet engines had entered active service and the airplanes had become high-tech machines. The wood industry and their customers see the importance of wood for the replacement of tropical timbers and chemical impregnated woods. Therefore wood modification is very important and in many places in the world, research on this topic has increased and commercialisation is developing very fast.

Wood acetylation

The process of wood acetylation has been known for many decades. The performance of the acetylated wood is excellent, in terms of dimensional stability, durability and UV resistance.

The quality of the acetylated wood can be measured by its acetyl content. And owing to this possibility, the performance of the wood can be guaranteed. The process does not harm the strength of the wood and does not add any chemicals which are not already naturally present in the wood.

The value of acetylated wood is not only coming from the performance of the wood but is also coming from values such as regular availability, consistent measurable quality, *etc.*

Titan Wood is the first company to produce acetylated wood on a large commercial scale. A commercial plant is being built in Arnhem, The Netherlands with a final capacity of approximately 24,000 m³ *per annum*.

The short-term goals for Titan Wood are to prove the commercial, large scale, process of acetylation and the production of acetic anhydride. Introduction and positioning of acetylated wood in the market on the right level, will make the production facility in Arnhem profitable.

The production of acetic anhydride and also wood acetylation are patented by Titan Wood. The long term goal is to license the technology to other companies worldwide who see the added value of acetylation. These companies can be wood production companies, processors of wood or others.

Because acetylation is difficult to pronounce and does not seem to be associated with wood or forests, a new name has been introduced for the acetylated wood: Accoya.

Accoya has the sense of a quality timber like Sequoia, the giant tree, and the first letters refer to acetylation. Also the name sounds like a "new wood species" which acetylated wood in fact is.

the market

To introduce Accoya into the market, it is very important to define target groups of customers. These target groups can be defined on different characteristics: needs and demands, turnover, application, geographic, *etc.*

The traditional segmentation of the wood market is as follows:

- Decking
- Garden wood
- Flooring
- Doors
- Windows
- Furniture
- Fuel
- Cladding
- Engineered wood products (plywood, OSB, MDF etc.)

Etc.

Within these segments, further defining is possible by size, risk-avoiding mentality,

Titan Wood has chosen its first target markets on performance characteristics needed in the final application. For example, if the wood is acetylated and is used for a fence post, only the durability is used and the other performances like the dimensional stability are not used. Because someone who wants to buy a fence post is not interested in something he doesn't use and is therefore more interested in a cheaper alternative.

Someone who produces an exterior door is using the durability, the dimensional stability and UV resistance (if transparent coated). A door producer is using all the performance characteristics. The added value on the door with glazing, paint and installing is large and therefore it is very important for a door producer to receive a consistent reliable quality of raw material. Here the possibility of measuring the acetyl percentage and the relating quality is a very important item which has never been possible before on natural wood species.

To position Accoya on the right (high) level it is important to introduce it into the right segments. The positioning of Accoya will be on a high level where aspects of reliability of high quality, consistent supply, low maintenance, and sustainability are the key drivers.

To position Accoya, the "first target markets" are chosen in the segments where the most values are used. This does not mean that the other segments are not important for the long-term strategy. For the introduction, Titan Wood is concentrating on the "first target markets":

- External doors and windows
- Cladding
- Decking

The companies we have targeted in these sectors are those who manufacture high quality products, are early adopters of new products and forward thinkers with companies of a size large enough to buy in bulk.

The Arnhem factory will introduce the acetylated wood with these companies and build a market by proving the quality and convincing the users of its superior quality. It is our view that the more "mass market" (higher volume) manufacturers will follow these early adopters as demand and supply grow.

relating industries

Because the acetylated wood comes to the market for the first time on a commercial scale, a lot of questions will arise regarding processing the wood in terms of gluing and coating. Also, Titan Wood is a not known player in the existing wood industry and therefore it is very important to have the support of relating industries who are known in the wood industry and support the introduction of Accoya.

Titan Wood has done, and is still doing, a lot of test programs with related industries such as coating and glue producers, to be able to advise the end-user on these items. Also many core target customers are involved in these testing programmes.

For the coating industry, there are new opportunities because the acetylated wood has become UV resistant and this in combination with the superior dimensional stability, a new generation of transparent coatings can be developed and introduced.

On the coating systems, the maintenance intervals can be increased because of the dimensional stability and also the UV stability of the lignin. This means that finally money can be saved on maintenance.

Also trials have been done to investigate the possibilities of powder coating on acetylated wood.

On gluing also, tests have been carried out to investigate the performance of different glues in combination with acetylated wood. Because of the change in characteristics of the acetylated wood, glues can behave differently and tests have shown that during the gluing process the parameters sometimes have to be adjusted. Because of the dimensional stability of the acetylated wood, the glue connections perform better in changing humid climates compared to non-acetylated wood.

Because of the new performances of Accoya, glue and coating producers are willing to co-operate and attach their name to Titan Wood and Accoya. This creates a synergy where both Titan Wood and the glue / coating producer can approach new customers or support current customers.

influencers and specifiers

Beside the directly involved industries, also the influencers and specifiers are important indirect target groups. These people are very important to create demand in the market by specifying the acetylated wood in building specifications. These influencers and specifiers are the architects, designers, local governments, etc.

In communication with these indirect target groups it will be emphasised that new designs can be created from Accoya which never have been possible before. For example, cladding material can be designed differently. Tests have shown that the boards can be thinner and wider without cupping or cracking. Accoya should not be used only as a replacement, but should be seen as a “new wood species” with new possibilities. Also, costs can be saved on maintenance during its lifetime. This is especially important with large buildings where the costs of maintenance are significant. After its lifetime, Accoya can be disposed as a normal wood, because there are no chemicals involved which are not already naturally present in the wood.

These indirect target groups are contacted by a direct approach and PR campaigns where they are informed by specialised media about this “new wood species”.

Good reference projects, such as the heavy traffic wooden bridges in Sneek, the Netherlands, are very helpful to show these people the advanced possibilities of Accoya.

The PR campaign is developed in such way that different “news worthy items” are placed in media which do reach the specific target group for whom the item is the most interesting.

Communication, branding

The website of Titan Wood and Accoya is the central point of all the communication. In all PR and other communications the receiver is directed to the website. On the website full information about Titan Wood and Accoya can be found. The advantage of a website is that everybody can reach it 24 hours a day and 7 days a week, all around the world.

The first questions can be answered by the list of frequently asked questions. Influencers and specifiers can download specification sheets to make it more convenient to specify Accoya.

Titan Wood will build a strong brand with Accoya. Wood modification is something relatively new and therefore new marketing tools can be used. Accoya is not only a “new wood species” but delivers more values, such as the quality measurement by measuring the percentage acetyl inside, consistent supply, sustainable wood, non toxic, etc. For example, a door producer or a decking producer can express in the final quality product by mentioning that there is “Accoya inside”.

The producer can differentiate himself from the standard wood species with this brand and should express this on the final product. This strategy is comparable with the “Intel inside” processor strategy in computers.

In different marketing campaigns, the logo and the brand values will be communicated. The values of reliability, high quality, low maintenance, sustainability and new technology will be expressed and communicated with the market.

- The industry is approached by Titan Wood directly together with the relating industries such as coating and glue producers.
- The influencers and specifiers are approached directly or by PR campaigns.
- The website of Titan Wood is informative and will contain information for all interested visitors.
- The Accoya brand is built on the website and PR campaigns.

Long term strategy and licencing the technology

With the factory in Arnhem, Accoya will be introduced mainly in Europe but also in some other continents.

The long term strategy is to licence Titan Wood's technology. A number of forest / wood industries have already shown interest in the Titan Wood technology and the first test programs have been set up.

These parties are interested to become a licensee of the Titan Wood technology in the future and will investigate the performance of the acetylation process on their wood species available. Also, test programs with their "core target customers" have been set up. Samples have been produced by the pilot plant in Arnhem and are used for testing.

With the production facility in Arnhem, the market is opened. The core target customers in the different segments have been able to differentiate themselves in the market and can show within their area how the product performs.

The licensees can supply their Accoya to "new" markets which they have never been able to supply with their natural wood produced. This new market does not cannibalise the markets they supply currently.

CONCLUSIONS

Titan Wood is the first company worldwide to introduce Accoya on a large commercial scale. The wood scientists and researchers are known with the acetylation process and do understand the value of it.

To some extent, the wood industry is known with this modification technique. It is the challenge for Titan Wood to create awareness of the people who don't know the acetylation process and Accoya. Also the industry has to be convinced that the Accoya is not just a "new wood species" but that it is a reliable, long term and sustainable solution for their needs. By a well constructed market approach together with the quality of Accoya and the right partners, Titan Wood is convinced that Accoya will become a success.

For more information please visit [<http://www.titanwood.com>]

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Prof. Dr. H. Miltz
Chairman organising committee